DETERMINATION OF CHLORINATED DIBENZO-P-DIOXINS AND CHLORINATED DIBENZOFURANS IN AMBIENT AIR

WORKSHOP PROCEEDINGS

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Proceedings of a Workshop
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DECEMBER 1992

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Preface

One of the most challenging tasks in analytical chemistry is the determination of the chlorinated dibenzo-p-dioxins (dioxins) and chlorinated dibenzofurans (furans) in real environmental samples. This is so because of the very low concentrations that must be detected and quantitatively measured, because it is very difficult to separate the dioxins/furans from other sample components that are present at much greater concentrations, and because only 17 of the 210 different dioxins/furans are considered to have appreciable toxicity.

The measurement of dioxins/furans in ambient air is of special importance, because the principal mechanism for the spread of these compounds in the environment is thought to be long-range atmospheric transport. For the past few years, Environment Ontario and Environment Canada have been working to develop effective methods of measuring dioxins and furans in ambient air so that their sources, transport, and fate in the environment can be studied. This work has been sponsored by the Canadian Council of Environment Ministers.

To share the results of this development work with the Canadian laboratory community, a workshop was held September 17, 1989 - to correspond with the 9th International Symposium on Chlorinated Dioxins and Related Compounds which was held in Toronto September 18-22. This report contains complete descriptions of the sampling and analysis methodologies that were discussed at the workshop.

Ray E. Clement
Toronto, Ontario
September, 1992

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Chapter 1

Ambient Monitoring for PCDDs/PCDFs: Critical Factors in Sampling Network Design

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SUMMARY

Much attention is presently focused on ambient PCDDs/PCDFs measurements in the vicinity of municipal solid waste incinerators. Typically a two-staged approach is employed consisting of ambient monitoring on both a pre-operational or background basis followed by a post-operational phase.

Sample collection and analyses procedures most often consist of high volume sorbent samplers in concert with high-resolution gas-chromatography/high resolution or magnetic sector mass spectrometry (HRGC/HRMS). While much has been written in the open literature on the subject of measurement methodology, little has been written about other critical factors in program and monitoring network design.

Critical factors or components in the design of state-of-the-art ambient monitoring networks for PCDDs/PCDFs in the vicinity of municipal solid waste incinerators are reviewed. Particular attention is focused on, but not limited to the following: monitoring network design, sampler placement criteria, siting criteria (both site specific and regional specific), meteorological parameters (wind speed, direction, temperature, barometric pressure, atmospheric stability class), sampling schedule, (frequency and duration), seasonal considerations, ambient background (What is it and how do we reliably establish it?) and quality assurance/quality control considerations.

INTRODUCTION

To date much of the data related to projected or predicted impacts of incinerator emissions on the multimedia environment (soil, water, air, biota, etc.) vicinal to these facilities has relied heavily on the use of measured or projected emission rates in concert with modelling (e.g., dispersion, deposition etc.) to predict ground level impacts. This has particularly been the case in the air permitting process associated with incinerators treating municipal solid waste in the

United States.

Little is known, however, about the levels or environmental burden of contaminants associated with incineration processes that may presently reside in the vicinity of these facilities. Furthermore, enhanced public sensitivity to potential health issues associated with all types of incinerators and a general sense of incredibility associated with exclusive modelling approaches provide further justification for the collection of state-of-the-art environmental measurements.

Ideally, this exercise would be a two-phased approach. Phase 1 would consist of a pre-operational or baseline environmental assessment conducted in and around the respective municipal waste incinerator prior to any potential influences posed by air emissions from the subject facility. Phase 2 would consist of an identical program conducted while the plant is in an operational mode as a means to assess any incremental changes in the multimedia concentrations of any of the parameters of interest. If the respective municipal waste incinerator is operational and a genuine pre-operational program is prohibited, it is essential that the sampling network contain sites for all media that are within and without predicted impact zones.

The resulting data product should be of well-defined quality such that it can provide a picture of environmental background ("what is background?") that is meaningful and tangible to the general public and perhaps allay uncertainties related to what quantitative impacts incinerators have (if any) on the vicinal environment.

While there is presently much interest worldwide in this subject, there is little in the way of formal guidance available pertinent to the design and conduct of these monitoring programs. The U.S. EPA does offer much in the way of general guidance for ambient monitoring but little of what is available is directly applicable to ambient monitoring for non-criteria or toxic air pollutants and more specifically PCDDs/PCDFs in the vicinity of stationary combustion sources. (1-6). Similarly, while much is available in the open literature pursuant to measurement of non-criteria air pollutants in the vicinity of municipal solid waste incinerators, little is provided related to program and network design considerations (7-18).

Accordingly, a comprehensive sample network/program design regime has been developed pertinent to both pre and post operational ambient monitoring in the vicinity of municipal solid waste incinerators. It makes use of available EPA guidance for air monitoring in the vicinity of stationary and area sources (1-5) and further incorporates the specific needs and objectives of numerous state and vendor sponsored pre-operational monitoring programs. It has evolved since that time as an integral component of numerous pre-operational ambient monitoring programs. In addition to PCDDs/PCDFs it is also directly applicable to a variety of other non-criteria air pollutants.

PROGRAM OBJECTIVES AND PRIMARY DESIGN CONSIDERATIONS

Perhaps the single most critical factor is the reply to the question *Why*? It is imperative that the program be designed and executed in strict accordance with one or more program objectives. In our experience, it is the program purpose or objectives which often receive the least amount of consideration until perhaps the program is near completion.

A summary of the more common general program objectives are provided in Table 1. Based upon our experience in the conduct of a number of pre-operational multimedia environmental assessment programs additional and more specific program objectives might include one or more of the following:

- Establish existing, baseline concentrations for target parameters in the vicinity of the municipal solid waste incinerator
- Establish what impacts, if any, the incinerator may have on these existing "baseline" levels
- Compare baseline data collected as part of this effort to concentrations measured at other similar locations in the United States
- Compare actual multimedia concentrations to influences predicted by conventional modelling such as is contained in the facility air permit
- Provide data suitable for incorporation into available Risk Assessment Guidelines for Resource Recovery facilities (e.g., assign exposure assessment for PCDDs/PCDFs using actual soil data in lieu of predictive deposition modelling data)
- Design a template program (e.g., statistically based design) that will serve as a model for use at other resource recovery facilities, and/or stationary combustion sources such as hazardous waste incinerators and sewage sludge incinerators.

Table 1: General Program Objectives

- MSW Permit Requirements
- Health Effects/Risk Assessment
- Regulatory - State "Air Toxics" Statues
- Model Validation
- Public Sensitivity (Modelling Credibility Issue)
- Liability Concerns

Attendant to these primary program objectives are a number of design features or characteristics of the monitoring program itself. The ultimate selection of program design features from those listed in Table 2 warrants a thorough understanding of the aforementioned program purpose and objectives.

Table 2: Program Design Considerations

- ❑ Monitoring Network Design/Site Locations
- ❑ Representative Picture
- ❑ Background/Reference Point
- ❑ Comparability of Pre and Post Operational Data
- ❑ Measurement Sensitivity - Commensurate with Existing Levels of PCDDs/PCDFs
- ❑ Data Reliability - Precision and Accuracy Goals (QA/QC)
- ❑ Multimedia Pathway Considerations - (Soils, Surface Waters, Biota, Vegetation)
- ❑ Redundancy in Sample Collection

Additional discussion of a selected number of critical program design features are provided as follows:

Monitoring Network Design - Spatial Orientation

Sampling stations should be spatially oriented about the incinerator so as to eliminate site-specific biases as well as provide stations suitable for continued post-operational monitoring. Make use of historical meteorological data as well as dispersion modelling contained in the Air Permit Application to identify maximum impact zones (e.g., TSP and particulate deposition isopleths). Conversely, stations not contained in the predicted plant impact zones will also be identified to serve as background sites.

Representative Siting/Sampling Network

It is imperative that the data product provide a representative picture of existing multimedia environmental burdens (soil, air, vegetation, biota, milk etc) in the vicinity of the respective incinerator. The program should be designed to provide data that are free from site specific and/or seasonal specific influences.

Additional considerations that constitute a representative measurement program are identified in Table 3.

Table 3: Considerations for a Representative Program

- ❑ Consistent with Program Objectives
- ❑ Freedom from Site-Specific Biases
- ❑ Seasonal Influences - Summer/Winter Extremes
- ❑ Spatial Orientation of Samplers
- ❑ Sampling Frequency
- ❑ Duration of Session
- ❑ Temporal Influences (Diurnal/Nocturnal Variability)
- ❑ Correlation w/Surrogate Parameters (Collocated TSP/Wind Rose w/Historical Data)

State of the Art Analyses to Provide Sensitivities Commensurate with Existing Levels of "Target" Parameters in the Environment

The monitoring techniques must be capable of assessing existing levels of environmental contaminants and in particular "target" compounds in the ambient atmosphere, soils, river water and bottom sediments in the vicinity of the proposed plant site. This is perhaps the most critical feature in the design of any pre-operational or baseline ambient monitoring program. The availability of actual measured values at this juncture in lieu of nondetected or "ND" values will permit a more defensible assessment of what impact, *if any*, plant emissions may have on air quality once the facility assumes an operational mode. This logic also precludes the "politically perceived notion" that environmental quality and in particular ambient air quality in the plant vicinity has been adversely affected should "ND" values result from the baseline monitoring program and state-of-the-art techniques, resulting in much lower yet measured values, be applied during post-operational monitoring.

The preferred approach consists of a variety of sample collection and analysis procedures that in our experience represent the state-of-the-art in analytical measurement. Most notably these include the use of X-ray fluorescence (XRF) for ambient trace metal measurements; use of hi-volume air samplers fitted with a sorbent "sandwich" (PUF/XAD-2) for the collection of ambient PCDDs/PCDFs, PAHs and PCBs; use of high-resolution or magnetic sector mass spectrometry for the unambiguous identification of TCDDs/TCDFs and other 2,3,7,8-substituted PCDDs/PCDFs (e.g., 0.01-0.1 pg/m^3 in air).

Data Precision and Accuracy - Quality Assurance/Quality Control

Each program must provide ample measures to ascribe precision and accuracy to the data product by means of an extensive *quality assurance/quality control function*. This includes but is not limited to the following critical items: collocated or replicate samples to provide a measure of the precision of the combined sample collection and analysis regime; field applied isotopically labelled surrogates for air samples as a means to assess analyte retention and/or breakthrough and ultimately a measure of accuracy; field blanks for each class of parameters as well as laboratory duplicates and spikes.

GENERAL SITING CONSIDERATIONS

General siting considerations are identified by means of an iterative review process involving the program objectives. These include but are not limited to a review of historical meteorological data vicinal to the facility as well as dispersion modelling (both ground level gaseous and particulate concentrations as well as particulate deposition isopleths). Additional siting considerations if required by the program objectives may include site selection on the basis of: population exposure assessment; multimedia pathways; and determination of background levels to provide a reference point for values collected in the vicinity of the facility itself. The latter category may include sites generally upwind of the facility and out of the maximum impact zone as predicted by dispersion or particulate deposition modelling. Urban, rural or marine locations not in the immediate vicinity of the incinerator may also be selected to provide data for eventual comparison with measurements collected in the general vicinity of the incinerator.

SITE SELECTION PROCESS

The site selection process consists of three tiers or levels of site selection criteria. The primary site selection criteria as listed in Table 4 are generally consistent with the general siting considerations identified earlier. Secondary siting criteria are consistent with U.S. EPA Guidance for PSD (Prevention of Significant Deterioration) monitoring of criteria air pollutants [5].

Table 4: Primary Site Selection Criteria

- ❑ Wind Rose Analysis - annual/Seasonal - Assign Predominant Vectors (Upwind/Downwind Site Disposition)
- ❑ TSP/PM_{10} Isopleths - Maximum/Minimum Impact Zones (Dispersion Modelling)
- ❑ Population Density - Demographics (Census Data)
- ❑ Background Determination (Urban, Rural, Remote Island)
- ❑ Multimedia Sampling Locations (Rivers, Lakes, Dairy, Soils, Etc.)

Tertiary site selection criteria or the third tier are comprised of practical or logistical considerations which are applied in the final stages of the site selection process, once the primary and secondary considerations have been identified, addressed, and optimally satisfied.

<u>**Primary Site Selection Criteria**</u>

<u>Meteorology</u>. The primary site selection criteria, as listed in Table 4, are applied after the program purpose and objectives have been identified. At a minimum the principal meteorological criterion in the site selection process is prevailing wind direction. Site locations are chosen along the wind vectors most prevalent in the area on an annualized basis as well as those in evidence

during the time(s) of year when pre or post operational monitoring will be conducted. The primary site selection criteria will include a review of historical meteorological data on a regional or site-specific basis (if available) in an attempt to identify sites predominantly upwind and downwind of the incinerator.

This exercise may consist of a review of computerized or "hard copy" National Weather Service data from the nearest monitoring station. A composite wind rose depicting wind speed and directional distributions and frequency data on an annualized or seasonal basis may be prepared and analyzed as a means to assign predominant vectors in the plant vicinity. A composite winter wind rose for the Bridgeport, Conn, Municipal Airport for the period 1965-1969 is illustrated in Figure 1.

Modelling (Dispersion and Deposition). Atmospheric dispersion or deposition modelling data such as contained in the air quality permit for the respective facility should be used to identify time weighted ground level impact maxima and minima as a function of direction and distance from the facility. This exercise should consist of a review of gaseous and particulate dispersion isopleths as well as particulate deposition isopleths. Particulate deposition isopleths such as those illustrated in Figure 2 (and in particular dry deposition data) are particularly useful in identifying maximum and minimum impact areas for pollutants that are primarily particulate associated such as PCDDs/PCDFs and metals. (Note: The strong particulate association of PCDDs/PCDFs in winter months is evidenced by the ambient particle/vapour distribution data plotted in Figure 3).

In this manner monitoring sites can then be located as close as possible to the maxima and minima within and without the plant's predicted influences.

Population Density - Demographics. Any assessment of population exposure will warrant a review of existing population distribution data. This may consist of either a relatively simple exercise in which residential areas in the immediate vicinity of the facility or the predicted impact zones (maxima or minima) are identified or a review of existing demographics data specific to the region or area in question.

Recent census data presented in tabular or optimally in graphical form such as a population density map are suitable tools to identify sites in populated areas.

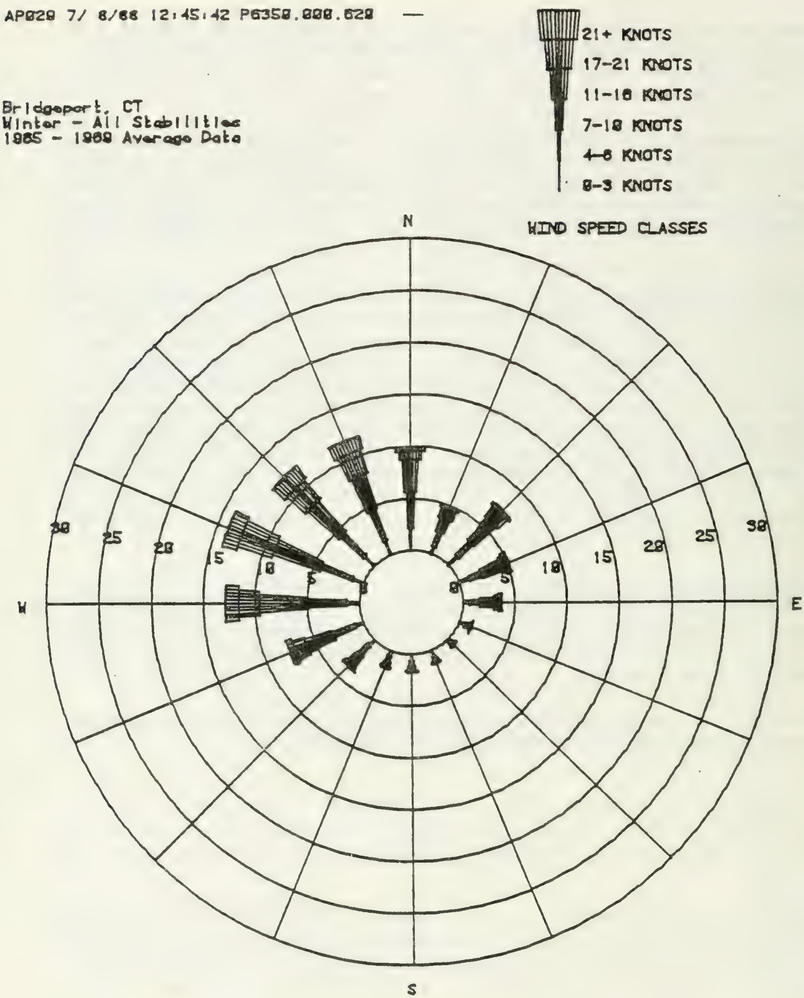

Figure 1: Winter Windrose - Bridgeport Municipal Airport

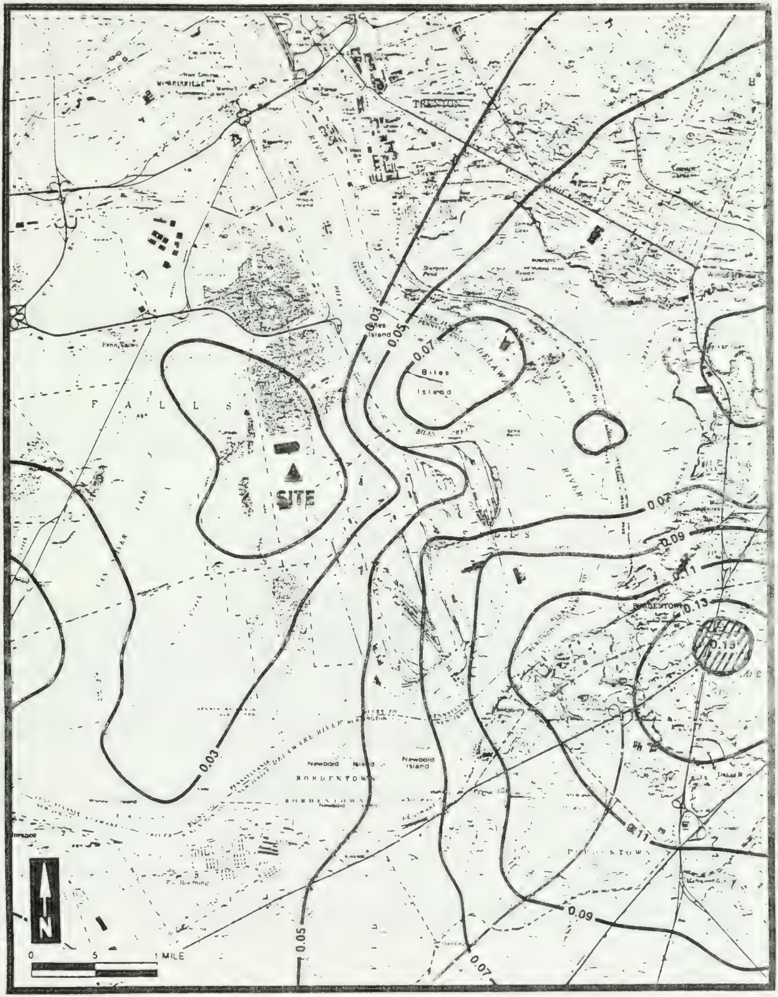

Figure 2: Particulate Deposition Isopleths - TSP/PM_{10} Annual Rates

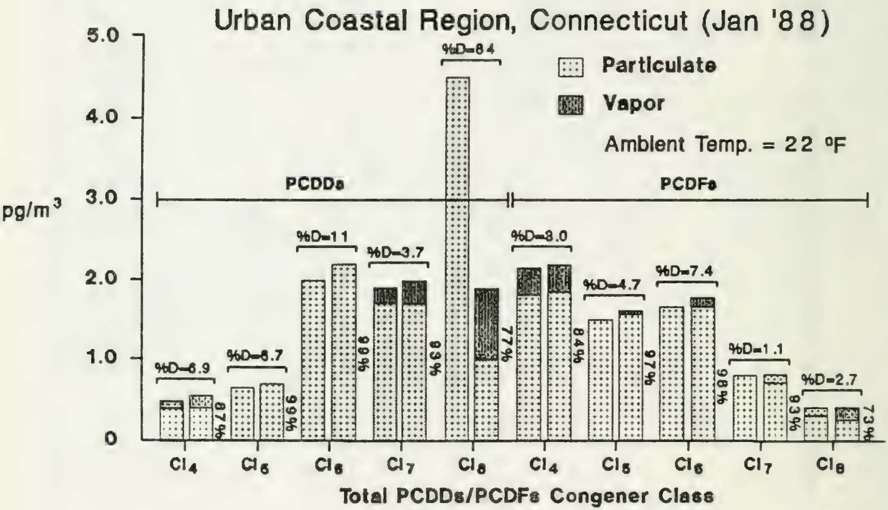

Figure 3: Particle/Vapor Distribution Data - Collocated Samplers

Background Determination. From an air quality perspective, background is a relative term generally considered to be a measure of the existing concentrations of the components of interest at a specific site or within a given geographical region. These concentrations are in turn a sum or aggregate of all source contributions (e.g., area, point, fugitive, etc.) other than that attributable to the source in question. In order to assess the incremental impacts of any area or point source on air quality in the site vicinity it is imperative that each of several types of background measurements be evaluated:

1. *Historical Background Data - Site Specific*
   This information generally consists of existing air monitoring data specific to the site in question. These data are generally suitable for comparison purposes, but due to disparities in seasonal, temporal, and meteorological parameters as well as incongruities in sampling and analysis procedures, it is not recommended that existing data bases *alone* be used to establish background concentrations at a given site. These data bases, if available, can provide some indication of existing conditions at the site/facility as well as the historical impact of site specific activities on air quality in the site vicinity.

2. *Historical Data Bases - Geographical Region*
   In addition to historical air quality data specific to the site itself, some consideration should be given to background data pertinent to the geographical region in which the site is located.

3. *Site-specific and/or Regional Background Data - "Real Time"*
   Naturally, the most important background measurements will be those that assess the relative contribution of the sources to existing air quality in the site vicinity.

In accordance with the site selection criteria offered earlier, background sites should represent, to the extent possible, each of three source classifications; namely rural, urban, and marine or remote. Actual monitors are placed within each region out of areas impacted by existing point sources or fugitive emission area sources.

Multimedia Sampling Locations. Multimedia environmental assessment programs by definition make use of aquatic and terrestrial based samples collected vicinal to the source.

Siting criteria for multimedia programs should make use of deposition modelling and other factors identified earlier in the selection of sites for sampling of the following matrices: soils, sediments, crops, fish, and dairy milk. Every effort should be made to place air quality monitoring stations in the vicinity of sites (e.g. soils) that have bene primarily identified employing particulate deposition isopleths. Figure 4 illustrates a multimedia monitoring network in which two of the three ambient monitoring stations have been collocated with soil and crop collection sites. Each of these sites were identified primarily using particulate deposition modelling.

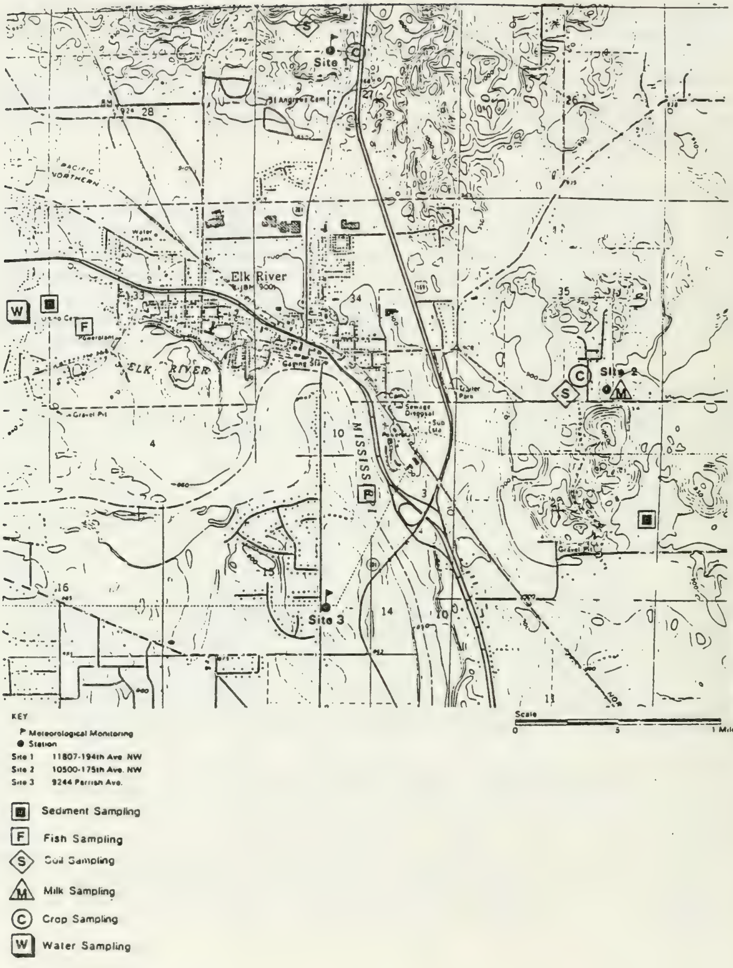

Figure 4: Monitoring Network Schematic - Location of Ambient Monitoring Stations in the Vicinity of the Elk River Resource Recovery Facility

Secondary Siting Criteria

Once a number of "candidate" sites have been identified employing the primary siting criteria, the site selection process continues with secondary siting or PSD compliance considerations. The secondary siting criteria generally are consistent with EPA PSD criteria and in particular as these apply to total suspended particulate (TSP) measurements [5]. The application of TSP siting requirements in the determination of ambient PCDDs/PCDFs for instance is a valid one due to the predominant association of these compounds with particulate matter in the atmosphere as previously demonstrated. A listing of the pertinent PSD compliance considerations employed here as secondary siting criteria is provided in Table 5.

Table 5: Secondary Siting Criteria - PSD Compliance (5)

Siting Characteristics	Distance Requirements
Height of sampler inlet above ground	2-15 meters
Distance of sampler from trees	>20 meters
Distance from sampler to obstacle	At least twice the height, obstacle protrudes above sampler
Unrestricted airflow	270° arc of unrestricted around sampler
Roof placement	2 meters from any wall, parapet, penthouse, etc., and no nearby flues that may significantly impact sampling
Highway	Based on PSD criteria for TSP

Site Specific Biases

Additional consideration must also be given to site specific biases which may positively influence or "distort" ambient concentrations at a given location. This is particularly critical in the case of trace PCDDs/PCDFs measurements which may be influenced by combustion and/or synthetic chemical by-products incident on a site-specific basis. Electric utility "rights-of-way" and "manicured" lawns should be avoided due to the potential for historical applications of PCDDs/PCDFs containing herbicides/pesticides. A listing of these and some of the more prominent site specific biases to avoid based upon ENSR's experience is provided in Table 6.

Table 6: Siting Considerations - Site-Specific Biases

- ❑ Mobile/Vehicular Sources
- ❑ Stationary Combustion Sources
- ❑ Stacks - Roof Top Locations
- ❑ Utility Right-of-Way - Herbicide Application History
- ❑ PCP Treated Lumber
- ❑ Natural Wind Erosion
- ❑ Lawns and Parks - "Manicured"
- ❑ Lawn Maintenance - during Sampling Session

Tertiary Site Selection Criteria

Once "candidate" sites have been selected on the basis of primary and secondary criteria actual sites are evaluated and selected employing a number of practical or logistical considerations. As listed in Table 7 these include availability of electrical service, site security and site accessibility. It is particularly important that each sampling location should be open to direct atmospheric deposition, with a minimum of vegetative canopy to provide a sample representative of maximum atmospheric particulate deposition.

To insure representative results, each site must be reasonably secure from possible tampering. This is accomplished by placing samplers away from crowded areas and inside a fenced or contained area. In addition, each site must be accessible for a reasonable length of time each day to allow the field team to efficiently conduct the monitoring program.

Final sample locations should be selected in secured areas (e.g., areas having limited or controlled access) and in areas not likely to be disturbed in the near future (e.g., conservation areas) to allow for representative post-operational sampling in the future, if required.

It should be noted that it may not be possible for all of these criteria to be met for each sampling point location. In this instance those locations which meet the majority of the indicated selection criteria will be identified as the selected sampling point(s).

Table 7: Tertiary Site-Selection Criteria
Practical/Logistical Considerations

- ❑ Electrical Service - 110V AC, 20 Amps Power (via Permanent Service or Portable Generator)
- ❑ Site Security - Void of Tampering and Vandalism
- ❑ Site Accessibility
- ❑ Post Operational Availability/Suitability

METEOROLOGICAL CONSIDERATIONS

Historical and Preoperational Meteorology

Meteorology plays a critical role in the design and ultimate execution of all ambient measurement programs. As identified in Table 8 meteorological considerations typically consist of both a review of regional meteorological data as well as the gathering of site-specific data coincident with the monitoring program. The regional meteorology can be best characterized through the use of historical data from a representative monitoring site near the facility location. Typically this will be a National Weather Service (NWS) station located at a nearby airport. NWS data are generally available as monthly summaries. Other sources also may be available and should be sought, especially in regions affected by complex terrain coastal weather regimes or other micro-meteorological influences. Meteorological measurements as part of the monitoring program are especially important in such regions because significant local variations in prevailing wind direction and ambient temperature may be common.

Table 8: Meteorological Considerations

- ❑ Historical Data Review - National Weather Service
  - Annual Wind Rose
  - Seasonal wind Roses
- ❑ Site Specific Meteorology
  - Permanent Tower
  - Portable System
- ❑ Meteorological "Screening" - Prior to Network Operation
- ❑ Data Correlation - Site Specific and Regional (NWS) Meteorology

In cases where representative historical data cannot be obtained, it may be necessary to conduct meteorological monitoring within the prospective air quality monitoring network area in order to provide the data needed for network design. This is termed as meteorological "screening" Such a meteorological monitoring program should be conducted over a period of at least one year to ensure that the data are not biased in favour of a particular season. Such data are optimally collected by means of a permanent or fixed meteorological tower (eg 10-30 m). However, portable meteorological stations situated at the appropriate height above ground level may also be substituted. If the monitoring data are to be input to an atmospheric dispersion model, EPA's *On-Site Meteorological Program Guidance for Regulatory Modelling Applications* should be followed to ensure that the resulting data are sufficiently accurate, precise, complete and representative to yield reliable modelling results.

A convenient meteorological data analysis applicable to monitoring site selection is the windrose - a tabular presentation that depicts the relative frequencies of occurrence of wind speed and direction and atmospheric stability. A graphical representation of a windrose can be used to select prospective monitoring site locations in the directions predominantly upwind and

downwind of the plant location. An example is shown in Figure 1. Both annual and seasonal windroses should be examined so that any significant seasonal peculiarities can be detected and accounted for in the seasonal monitoring strategy.

Site Specific Meteorology - Critical Parameters

The collection of site specific meteorology is a requisite in the conduct of the actual baseline assessment program. At a minimum, horizontal wind speed and direction data should be gathered on a continuous basis. Ambient temperature (°C) and barometric pressure data should also be collected on a periodic basis throughout the course of each sampling session. It is also advisable to have "ready" access to precipitation (eg rainfall) and atmospheric stability class data. Precipitation measurements should be made directly on the site or in the site vicinity if representative National Weather Service data are unavailable. Atmospheric stability class data are generally based upon the standard deviation of horizontal wind direction or via other performance equivalent methodologies. A summary of these critical meteorological parameters and associated. EPA sanctioned performance criteria (precision errors) are provided in Table 9.[1]

Table 9: Critical Meteorological Parameters (1,3)

- ❑ Wind Direction - Horizontal (Continuous; Precision Error <5°)
- ❑ Wind Speed - Horizontal (Continuous; > 0.5m/s Threshold)
- ❑ Ambient Temp. (Precision Error < 0.5°C)
- ❑ Wind Rose(s)
  - Sampling Periods(s) - Diurnal
  - Program Composite - Nocturnal
- ❑ Atmospheric Stability Class
- ❑ Precipitation
- ❑ Barometric Pressure

In addition to site-specific meteorological monitoring personnel should establish direct verbal contact with a nearby permanent weather station such as a local airport. This will serve a number of critical purposes:

- ❑ Provide additional information to supplement on-site meteorological data. This can serve as a quality control function for the site specific data by assessing both accuracy and precision of selected parameters.
- ❑ Regional meteorological data such as that available from a nearby airport can also fill in data gaps created by operational problems, malfunctions and data inconsistencies associated with the site specific system.
- ❑ Provide much needed data on critical parameters typically not available from portable meteorological systems such as precipitation, atmospheric stability class

assignments and relative humidity.

DURATION OF SAMPLING SESSION

Ambient PCDDs/PCDFs measurements are typically collected on a time-weighted (TWA) basis or over an integrated period consistent with one or more of the criteria identified in Table 10. PCDDs/PCDFs sampling sessions may simply be 24 hours in duration so as to be consistent with the requirements of the EPA or National Air Sampling Network (NASN) 6-day schedule for measurement of Total Suspended Particulate. Alternatively, shorter sampling periods may be selected so as to be consistent with averaging times for toxic air pollutants put forth by the oversight regulatory agency or perhaps a sampling period of 48 hours or greater (eg 72 hrs) to provide greater air volumes and hence optimization of analyte sensitivities.

Table 10: Considerations for Sampling Frequency/Duration

A. Frequency/Schedule
- ❑ Seasonal Campaigns
- ❑ EPA NASN Schedule - TSP/PM-10 (Every 6th Day)
- ❑ Collocated Surrogate parameter
- ❑ Multimedia Sampling Schedule

B. Duration
- ❑ Regulatory AAL Averaging Times - 24 hrs; 8 hrs
- ❑ NASN Schedule/TSP - 24 hrs
- ❑ Optimum Sensitivity - 48 hrs or Greater

QUALITY ASSURANCE/QUALITY CONTROL

The monitoring program must be designed to result in measured values that meet or exceed data quality objectives for precision and accuracy identified in the program design phase.
The resultant data product must be of well defined quality such that it can provide a picture of environmental background ("what is background") that is meaningful and tangible to the general public and perhaps allay uncertainties related to what quantitative impacts incinerators have (if any?) on the vicinal environment.

Further, the final data product should be "representative" of the environment in question and suitable for comparison to predictive data historically provided using conventional modelling approaches.

As discussed previously precision and accuracy will be ascribed to the data product by means of a comprehensive quality assurance/quality control regimen. Specific features of the QA/QC

regimen in particular as it applies to ambient PCDDs/PCDFs measurements include the following:

1. *Collocated Samples*

   Collocated samples provide a measure of precision for the combined sample collection and analysis regime. Comparison of results from continuous versus wind-directionally controlled samples can also assist in data interpretation at sites impacted by multiple sources or characterized by intermittent or irregular releases. Refer to Figure 5 for typical ambient PCDDs/PCDFs data generated using collocated PS-1 samplers.

2. *Field Applied Surrogates*

   Isotopically labelled PCDDs/PCDFs congeners applied prior to sample collection as a means to assess analyte retention and/or breakthrough. These data ultimately provide a measure of accuracy for the combined sample collection and analysis regime. A summary of field applied surrogate data noting % recovery data for a variety of PCDDs/PCDFs congeners at a number of fortification levels is provided in Table 11.

Table 11: Summary of Field Surrogate Results

	50 pg fortification		200 pg fortification		500 pg fortification	
	mean % recovery	std. dev.	mean % recovery	std. dev.	mean % recovery	std. dev.
^{37}Cl-TCDD	110	8.1	84.6	9.3	105	21.8
$^{13}C_{12}$-TCDF	112	15.6			97.7	15.6
$^{13}C_{12}$-PeCDF			108	12.5		
$^{13}C_{12}$-HxCDF	103	6.4	109	13.8		
$^{13}C_{12}$-HxCDD			109	20.9		
$^{13}C_{12}$-HpCDF			85.3	15.6		

3. *Field Biased Blanks*

   These are employed to assess spurious contamination that may arise during field handling and transport of samples. It is particularly important that the field blanks be handled in such a way that the contribution of passive particulate deposition (if any) to PCDDs/PCDFs levels in actual samples be addressed. Further discussion of this issue as well as a more comprehensive treatment on the role that quality assurance/quality control must play in the validation and interpretation of ambient PCDDs/PCDFs data is presented elsewhere by this author [19].

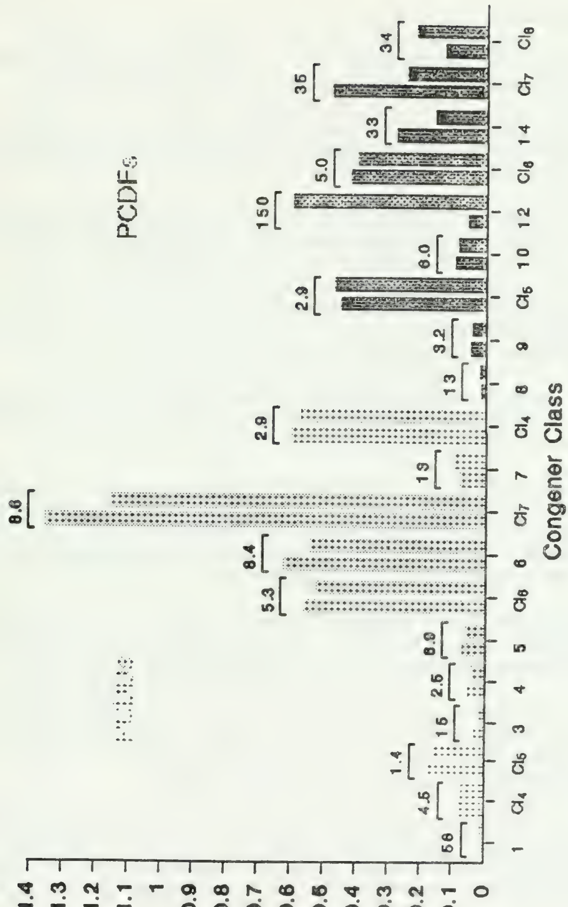

Figure 5: Collocated Sampler Data

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Chapter 2

High Volume Air Sampling Methods for PCDD/PCDF

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SUMMARY

Current ambient air sampling methods for dioxins and furans use either a General Metal Works Model PS-1 low volume air sampler (300-850 m^3 per 24-48 hours) or a modified high volume sampling motor(1000-2000 m^3 per 24-48 hours). Both types of samplers are used with a filter (either glass fibre filter or a Teflon coated glass fibre filter) to trap particulate bound dioxins and furans, followed by a polyurethane foam plug (PUF) to trap vapour phase dioxins and furans. The systems allow for femtogram per cubic meter detection limits for tetra- to octa-dioxins and furans. The systems used by Environment Ontario, Environment Canada, and ENSR Consulting and Engineering are described in detail.

INTRODUCTION

In recent years, public concern regarding toxic air pollutants in the atmosphere has brought about the need to perform ambient air measurements for polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). PCDD/PCDF are considered semivolatile compounds and can occur in the atmosphere both in the particulate phase and the vapour phase. Therefore, modification of a direct filter collection technique was necessary. In addition, due to the extremely low concentrations of these compounds in ambient air and their potentially high toxicity, very large sample volumes are necessary to optimize analytical detection limits. This has led to the development of various collection devices and collection media for sampling PCDD/PCDF.

Sample collection devices consist of a motor and collection media support housed in an

aluminum shelter. Air is drawn through the collection media by the motor and exhausted at some distance form the shelter to avoid re-sampling of exhausted air. The collection media is held in its housing by means of a wire mesh support. The samplers also have timers for controlling the sampling events and a gauge or gas meter to measure flow.

The sample collection media, as mentioned before, consists of a filter for the particulate bound material and an adsorbent material for the vapour phase PCDD/PCDF. The filters used are either glass fibre filters or Teflon-coated glass fibre filters. Today, the most commonly used adsorbent material is PUF, however, adsorbent materials such as silica gel, XAD resins, and Florisil have been used. Although silica gel is easy to clean, handle, and extract, one of the drawbacks of this adsorbent is that only low volumes of air can be drawn through the sampler; this limits the detection limits that are achievable. Silica gel's performance is also humidity sensitive. XAD resins are difficult to clean and handle and are generally not used.

PUF is the adsorbent currently used by most agencies. PUF is inexpensive (regular upholstery grade materials can be used), is easy to handle and to pre-clean using Soxhlet extraction, has relatively low background interferences and has a high retention efficiency. The foam also provides less flow resistance and is hydrophobic, which means that high humidity and precipitation do not interfere with the sampling. PUF is used by Environment Canada, Environment Ontario, United States Environmental Protection Agency, ENSR Consulting and Engineering, and other agencies.

ONTARIO MINISTRY OF THE ENVIRONMENT

Sampler Selection

Due to the very low levels of PCDD and PCDF in ambient air, the primary objective was to select an instrument capable of sampling a large volume of air over a reasonably short time frame. A standard high volume (HiVol) sampler, modified to accept a vapour trap, was selected (Figure 1). For a given duration, the modified HiVol samples a larger volume of air than the commercially available PS-1 and thus lower detection limits are achieved for a specified analytical technique. The sampler described here compares favourably with a similar instrument used by Environment Canada (Tashiro et al., 1989).

Modifications to the sampler include: the filter hold-down frame is made of cast aluminium with a double silicone gasket on the underside and a flat top to prevent the wing nuts from slipping off the frame when they are tightened down (Figure 2); an aluminium cartridge is added to the sampling train below the filter horn to hold a polyurethane foam (PUF) plug (Figure 3); and a dry gas meter is attached to the downstream end of the PUF cartridge to measure the sampled volume.

Experiments involving single and dual PUF plugs indicated no breakthrough from the upstream PUF to the downstream PUF for sampling times up to 72 hours (Tashiro et al., 1989). Thus the routine operation of the sampler with only a single PUF cartridge is confirmed.

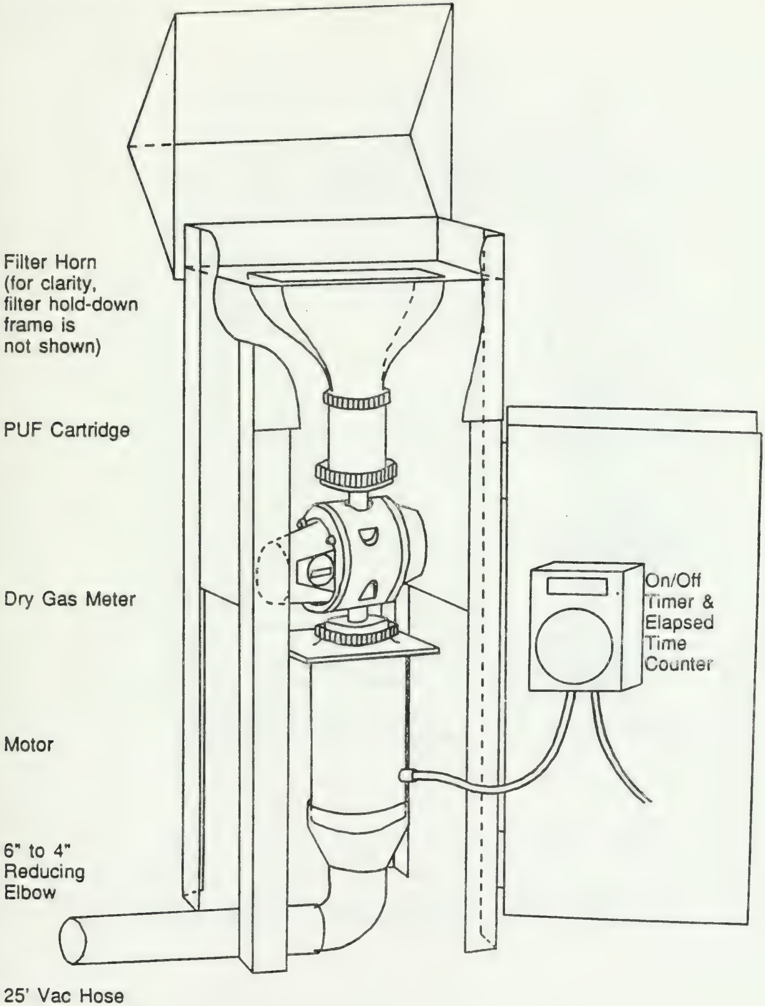

Figure 1: Environment Ontario: Ambient Air PCDD/PCDF Sampler

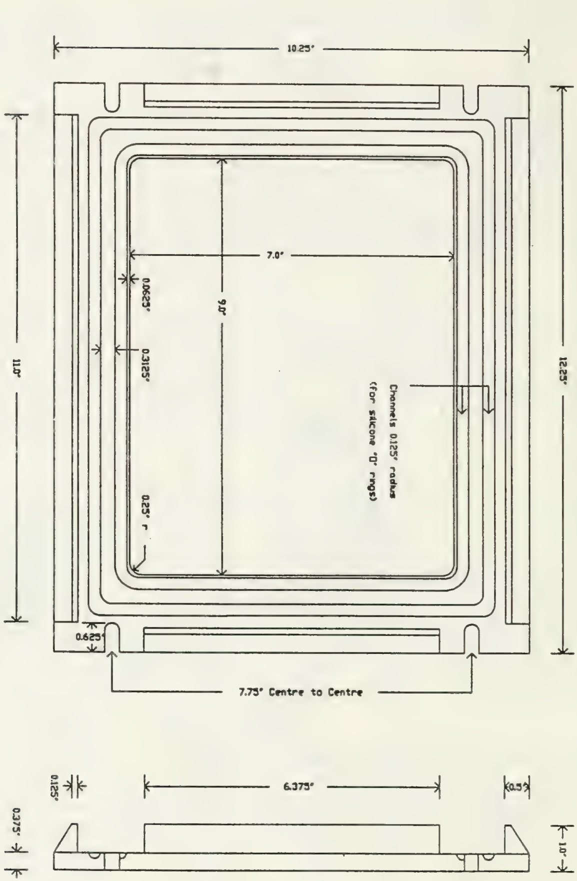

Figure 2: Environment Ontario: Cast Aluminum Filter Hold-Down Frame

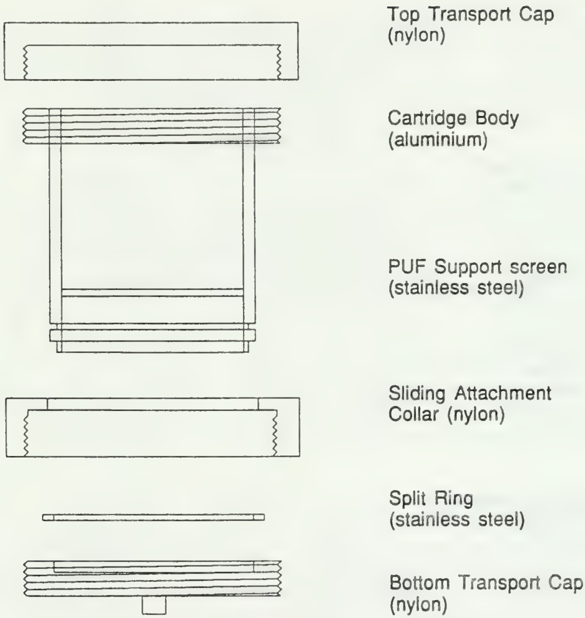

Figure 3: Environment Ontario: Cartridge for Polyurethane Foam Plug

Industrial vacuum hose is used to vent the motor exhaust away from the sampler to prevent re-sampling exhaust air. The sampler is operated at full line voltage without a flow controller and, depending upon the resistance of the PUF, flow volumes range between 20 and 40 cfm. The sampler is operated for 48 hours to yield a sample volume of between 1600 and 3200 cubic metres.

Initially, the cartridge was made entirely out of aluminium. This caused significant problems with binding, particularly in the wintertime. The upper and lower transport caps and the floating collar are now made from nylon and binding is not a problem. Removing the split ring allows the floating collar to be replaced as the threads get damaged with use.

Sampling Protocol

Two HiVol shelters are installed at each site; one for the active sample and one for the passive sample. Clean equipment is shipped from the laboratory to each field site in picnic coolers. Each site receives two cartridges with PUF plugs, three filters, and a cleaned filter horn. The third filter is a spare in case a filter is mishandled during installation. The cleaned filter horn is used for the active sample; the filter horn from the passive sampler is cleaned quarterly. During sampling, the top and bottom transport caps from the PUF cartridges are stored in the cooler.

When the sample is removed, the filter is folded in half with the exposed side in and wrapped in aluminium foil and placed in a zip-loc bag. The transport caps are screwed tightly onto the PUF cartridge with the upper gasket and lower o-ring in place to effect a tight seal. The PUF cartridges, folded filters, and the filter horn from the active sampler are placed in the cooler and shipped to the laboratory for analysis (sample) and cleaning (filter horn).

Sample Documentation

All details regarding the collection of a sample are recorded on a single form which meets the requirements of both the analytical staff and the program coordinator (Figure 4). The top section of the form contains information required by the laboratory for tracking the sample through the analysis, billing the correct project, and distributing results to the correct client(s). The middle section of the form contains information pertinent to the collection of the sample. Regional technicians provide Field Sample Number, Sample Date, Station ID Number, and the actual sampling information: elapsed time, rotameter and/or dry gas meter readings, the instrument number and the sampled volume. This sampling information is merged with the analytical results in a database such that all details of each sample collected are readily available. The bottom section of the form provides an opportunity to add further comments regarding the collection of the sample. Such information as power outages, dropped or torn filters, etc. is recorded here.

Summary

A description of the sampler, the sampling protocol, and the sample documentation is provided in Ontario Ministry of the Environment Polychlorinated Dibenzo-*p*-Dioxin and Polychlorinated Dibenzofuran Monitoring Network Standard Operating Procedures and Technical Manual, Report

DIOXIN / FURAN SAMPLING PROGRAM
SAMPLE SUBMISSION/HISTORY FORM

SUBMISSION NO.: ______________ SAMPLE PROGRAM CODE: 02 004 04

LAB: TR PRI: N FD TYPE: ____ SAMPLING AGENCY: 01 02 02 05 01 DATE SUBMITTED: ___/___/___

REGION: _____ TELEPHONE: _________ PRIMARY CLIENT CODE: AR019 COPIES TO: CLD03 / CLD06 /_____/_____

FIELD OPERATOR: __________________ SUBMITTED BY: ________________(print)________________(sign)

FIELD SAMPLE NO	SAMPLE TYPE	LABORATORY SAMPLE NUMBER	SAMPLE DATE dd/mm/yy	STATION ID NO.	REMARK CODE	TEST GROUP	ELAPSED TIME COUNTER	TOTAL MINUTES	DRY GAS METER READING	VOLUME (m³)	FIELD COMMENTS
	PU					PEDIOX	START		START		
							END		END		
	PU					PEDIOX	START		START		
							END		END		
	PU					PEDIOX	START		START		
							END		END		
	PU					PEDIOX	START		START		
							END		END		
	PU					PEDIOX	START		START		
							END		END		
	PU					PEDIOX	START		START		
							END		END		

SPECIAL REMARKS:

Original to MOE Lab   1 Copy to Program Coordinator   1 Copy to Region

Figure 4: Environment Ontario: Sample Submission/History Form

No. ARB-225-89. The first page of the Table of Contents of this document is shown in Figure 5. Document control protocol closely follows that of the U.S. EPA; title, section, revisions, date, and page information recorded in the top right corner of every page.

ENVIRONMENT CANADA

Environment Canada has been involved with the development of a PAH/Dioxin sampler since the early eighties. At that time, there were no commercially available instruments for this type of air sampling. Environment Canada began this project by modifying a high volume sampler for suspended particulates. This section describes the sampler and its operational procedures.

Basic Requirements for the Sampler Design

It was decided that the sample canister would have a 15 cm foam bed consisting of two 75 mm diameter cylindrical plugs of 75 mm thick PUF. The 75 mm foam was available commercially. This arrangement provided the possibility of studying break-through volumes by analyzing the front and back foams separately. The modification of a high volume sampler also provided ease of operational support, since most of the field staff were familiar with the sampler. The sampler was designed to have maximum air flow rate to increase its sensitivity. The operational procedures were designed to minimize sample contamination throughout the sampling process, which includes the transport of canisters to the site and their return to the laboratory for analysis.

Description of the Environment Canada Sampler

After a few experiments, the configuration of the sampler was finalized as shown in Figure 6. A regular high volume sampler was modified by adding a sample canister immediately below the filter holder head. At the exit of the canister, an adaptor was designed to direct the exit air to a dry gas meter outside of the sampler enclosure. The motor was located outside the housing to prevent heating of the sample canister. Experiments had shown that the heat generated by the motor could raise the temperature of the air around the canister by 15° to 20° C. The collection efficiency of the PUF plug decreases in this elevated temperature condition. Placing the motor downstream of the dry gas meter also eliminates the possibility of back diffusion of inherent contaminants in the motor to the back foam plug of the canister.

The PUF canister is shown in Figure 7. It consists of an aluminum outer casing with an inner glass liner in which the foam plugs are inserted. The glass liner is supported on both ends by Teflon rings. Viton O-ring seals are used between the Teflon and the glass. A stainless steel screen supports the foam plug at the downstream end of the glass lining. During transportation to the field and back to the laboratory, the canister is capped by two Teflon plates and gaskets held in place by aluminum cap rings.

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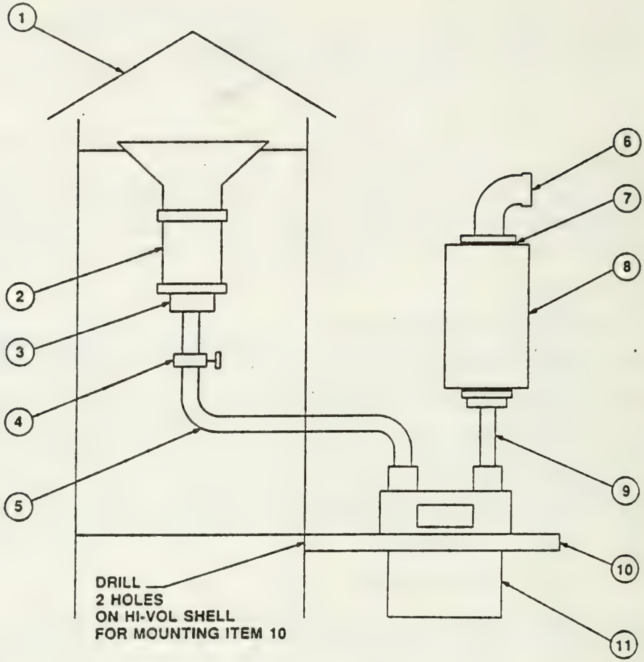

1. Hi-vol Sampler Shell with Control Timer & Pressure Sensor
2. PUF Canister Assembly Drawing #1001
3. Canister Adaptor Drawing #2001
4. Connector Drawing #2010
5. S-Pipe Assembly Drawing #2020
6. Pipe Elbow & Flange Drawing # 2030
7. Rubber Gasket Drawing #2040
8. Hi-Vol Motor Housing Drawing #2050
9. Motor Adapter Drawing #2060
10. Gas Meter Support Bracket Drawing #2070
11. Gas Meter Rockwell Model RCM415TC

Figure 6: Environment Canada: PAH/Dioxin Sampler Assembly

Operation Procedures for the Environment Canada Sampler

The sensitivity of the sampling procedure requires that the operator must wear disposable gloves of either polypropylene or cotton during the installation and removal of the canister. Installation of the canisters is usually done inside a protected shelter to make the task easier for the operator. The filter holder head is removed from the sampler and assembled with the canister and the adaptor with the assistance of strap wrenches. The entire unit is then placed back on the sampler. The connection between the adaptor and the dry gas meter is made by a quick connect clamp. The cap rings and the end plates of the canister should be wrapped in clean polypropylene bags for re-use after sampling.After the canister is installed, the sampler must be checked for any air leakage to ensure a good installation has been accomplished. A piece of Tedlar sheet is placed on the filter holder instead of the particulate filter. The motor of the sampler is activated for 30 seconds for it to stabilize. The test dial on the dry gas meter is timed. If the flow rate indicated by timing the test dial is below 0.01 cubic meter per minute, the system is considered acceptable for sampling. The Tedlar sheet is then replaced by the particulate filter used for sampling.

Since the dry gas meter is operating under vacuum, the indicated volume is corrected by using the vacuum readings obtained from the two vacuum ports provided at the inlet and at the exit of the meter. The operator must measure the inlet and exit vacuum before sampling, by activating the motor after the system leak check is completed. After the vacuum readings are taken, the sampler is set for sampling time and date as per a normal high volume sampler. The appropriate information is then entered on the data sheet.

When sampling is completed and before the removal of the particulate filter and the canister, the motor is again activated for 30 seconds to obtain the vacuum readings at the inlet and exit of the gas meter. The particulate filter is removed and folded once. It is wrapped in pre-cleaned aluminum foil and sealed by turning up the edges and placed in a polypropylene envelope. By releasing the quick connect clamp, the complete canister and filter holder head is removed. The assembly can then be take into the shelter and disassembled with the aid of strap wrenches. The canister is re-capped and sealed with the original caps and Teflon plats. The data sheet is checked for completion and is sent with the canister to the analytical laboratory. If the ambient pressure readings were not available at the station, they can be obtained from the nearest weather station. A typical data form is shown in Figure 8.

ENSR CONSULTING AND ENGINEERING

ENSR Consulting and Engineering has conducted numerous monitoring programs over the past 7 years to measure levels of PCDDs/PCDFs in the ambient atmosphere. With this experience, ENSR has developed air sampling techniques and procedures using commercially available materials which optimize the collection and quantification of trace levels of each of the 2,3,7,8-substituted PCDD/PCDF congener classes. In the performance of these programs, sample collection is accomplished by use of glass fibre filter and polyurethane foam (PUF) sorbents in conjunction with General Metal Works model PS-1 samplers. Typical operating

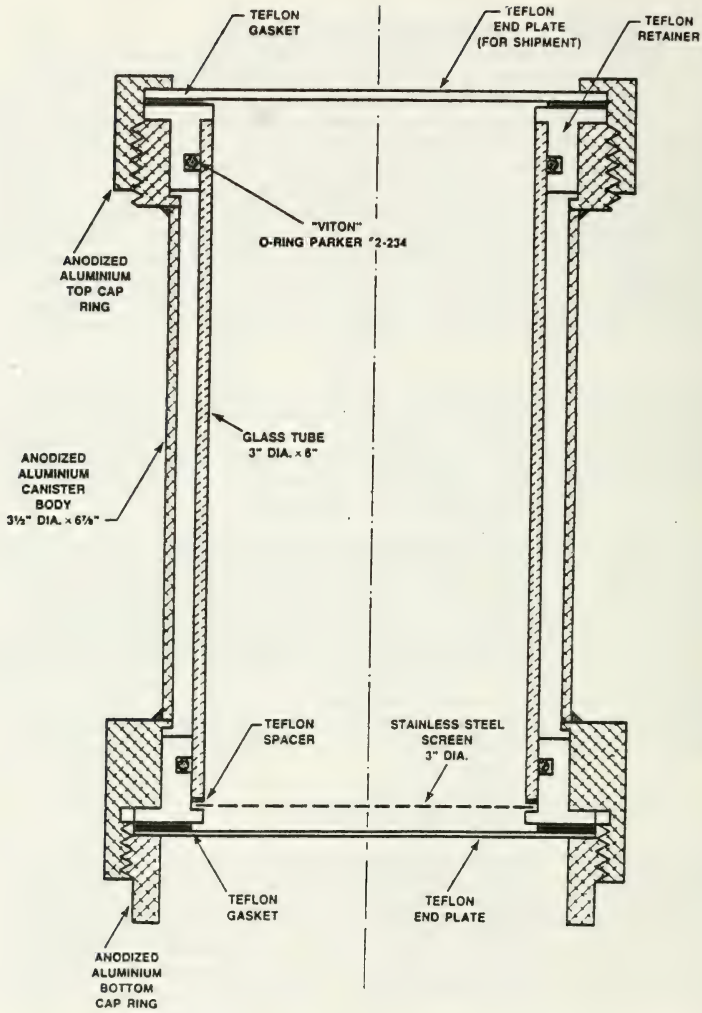

Figure 7: Environment Canada: Polyurethane Foam Canister Assembly

SAMPLER LOCATION ____________________ SAMPLER NO. ____________________

Canister & Filter No. 1	Date Installed 2	Initial Gas Meter Inlet Vacuum in Hg 3	Initial Gas Meter Exit Vacuum in Hg 4	Initial Gas Meter Reading (m^3) and Elapsed Time 5	Date Sampled 6	Date Removed 7	Final Gas Meter Inlet Vacuum in Hg 8	Final Gas Meter Exit Vacuum in Hg 9	Final Gas Meter Reading (m^3) and Elapsed Time 10

SAMPLING DAY TEMP. HI: ________ LO: ____________ SAMPLING DAY ATMOSPHERIC PRESSURE: __________ kPa

OPERATOR: ______________________________ DATE: ______________________________

REMARKS: ____

Figure 8: Environment Canada: PAH/PCB Dioxin Sampling Data Sheet

specifications include a 24-48 hour sample collection duration at sample flow rates of 200-300 liters per minute resulting in total sample volumes of approximately 300 to 850 cubic meters. By following these procedures, in conjunction with analysis by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS), detection limits in the femtogram per cubic meter (fg/m^3) range for each of the 2,3,7,8-substituted PCDD/PCDF congener classes can be consistently achieved.

This section describes some of the details for the collection of PCDDs/PCDFs by these techniques including sorbent selection, sampling equipment description and sorbent specifications, sampler calibration, sampler operation and siting requirements.

Selection of Sorbent Materials

As mentioned earlier, glass fibre filters alone are not adequate for the collection or retention of PCDDs and PCDFs. However, several types of sorbent materials have been found to be effective for retention of semivolatile organic compounds in air including dioxins and furans. These materials include such sorbents as silica gel, florisil, XAD resins and PUF. ENSR has found that a two stage collection technique involving a glass fibre filter in conjunction with PUF has several advantages over other sorbents for sampling PCDDs/PCDFs in ambient air. In this arrangement, the glass fibre filter stage collects particulate related PCDDs and PCDFs. PCDDs and PCDFs which exist in the vapour state, or that are not retained by the glass fibre filter are collected on the PUF sorbent stage.

Sampling Equipment Description

The PS-1 sampler is a commercially available sampler manufactured by General Metal Works Inc. of Village of Cleves, Ohio. It is a modified high volume TSP sampler which is designed to make use of a two-stage filter/sorbent sample collection device and is based on early SURC sampler collection concepts. The PS-1 was originally marketed to sample ambient air for organochlorine and organophosphate pesticides. It is capable of operating for extended periods of time at flow rates up to 300 liters per minute. Although other sampling arrangements are available or can be manufactured, ENSR uses the PS-1 primarily because it is readily and commercially available, spare parts and supplies can be obtained quickly, it is a standardized system, and it is less bulky and more transportable for short-term measurement programs than some other samplers in present use. A schematic of the PS-1 sampler is provided in Figure 9.

The operation of the sampler is as follows. Ambient air is drawn through the glass fibre filter and PUF module by a by-pass blower motor equipped with a voltage variator, flow control valve and venturi to control and measure the sample flow rate. Pressure taps on either side of the flow venturi are connected to a 0-100" H_2O magnehelic differential pressure gauge for flow rate measurement. The sampler is also equipped with a non-resettable elapsed time indicator and a seven-day on/off sample period timer.

The dual chambered sampling module containing the glass fibre filter and PUF sorbent is

shown in Figure 10. The upper portion of the module is used to hold a four inch diameter glass fibre filter between two teflon gaskets. The threaded lower portion of the module contains a removable glass cartridge which contains the PUF sorbent material. The glass cartridge and PUF sorbent are depicted in Figure 11.

All of the glass cartridges used by ENSR are engraved with a unique identification number for sample identification. In addition, ENSR purchases bulk sheets of 3-inch thick polyurethane foam from a foam manufacturer. From these sheets, ENSR cuts PUF plugs which are a slightly larger diameter than the outside diameter of the glass cartridges to prevent channelling of sample gas around the PUF should shrinkage occur during sample collection. The foam plugs are fitted into individual glass cartridges and are then sent along with the glass fibre filters to the analytical laboratory for extraction, clean-up and surrogate spiking prior to sample collection. The cleaned, prepped and spiked cartridges and filters are returned from the laboratory wrapped in pre-cleaned aluminum foil and packaged in zip-loc bags.

Sampler Calibration

The PS-1 sampler is calibrated on a regular basis and the calibration is checked before and after each sample is collected. Calibration is accomplished by use of a specially designed calibration orifice and water manometer. The calibration orifice is certified annually by calibration with a primary standard (Roots Meter).

The calibration sequence involves placing an empty glass cartridge into the sample module and connecting the calibration orifice to the filter holder assembly. A 0-8 inch water manometer is then connected to the pressure tap in the calibration orifice device and the system is turned "on", and leak-checked. The sampler is then calibrated at 5 points which cover the full range of the magnehelic flow indicating gauge. Each calibration point is set by adjustment of the flow control valve or voltage variator. At each of the 5 calibration points the magnehelic gauge and manometer inches of water are recorded. Using this information as well as the ambient temperature, the barometric pressure and the orifice calibration data, a calibration curve is developed based upon magnehelic gauge readings versus flow rate in liters per minute at standard conditions. This curve is later used to determine sampler flow rate and sample volumes based upon magnehelic gauge readings recorded during the sample collection period.

Sample Collection Specifications and Operation

In order to optimize the lower limit of detection for PCDDs/PCDFs in ambient air samples, total sample volumes must be maximized without exceeding the sample volume at which sample breakthrough may occur. Typical operating specifications for the collection of PCDDs/PCDFs using the PS-1 sampler, therefore, include a sampling duration 24-48 hours at a flow rate of 200-300 liters per minute resulting in a sample volume of approximately 300 to 800 cubic meters.

The typical sample collection sequence of events is summarized in Table 1. First, an initial sampler calibration check is performed by attaching the calibration orifice to the sampler and performing a calibration check at two or more points which bracket the anticipated sample flow rate. This calibration check is performed as described in the calibration procedures described earlier. An initial leak check is also performed. If the calibration check does not agree within 10% of the sampler calibration curve, then the calibration curve is considered invalid and a new calibration must be performed.

Following the completion of the calibration check, the sampling module is cleaned and rinsed with acetone and allowed to dry for several minutes. The sorbent cartridge and filter are then carefully removed from their packaging and loaded into the cleaned sampling module. This must be done while wearing clean, cotton gloves to avoid any possible sample contamination. The aluminum foil wrapping is carefully folded and placed into the zip-loc bag, sealed and retained for repackaging the collected sample. The field blank cartridge and filter are also carefully removed from their packaging using the same procedure, and are placed aside while completing the rest of the startup procedure. Next, the seven-day "on/off" timer is set, the elapsed timer reading is recorded and the sampler is started. After waiting approximately 5 minutes, the initial flow rate is set by adjusting the flow control valve or the voltage variator, and the initial flow indicator (magnehelic gauge) reading is recorded. At this time the field blank is recovered by carefully placing the filter into the glass cartridge, re-wrapping the cartridge with the aluminum foil and resealing it in the zip-loc bag. If possible, the sampler should be checked one or more times during the sample collection period to record the flow indicator reading. This is especially important during longer sampling periods (greater than 24 hours) or when heavy particulate buildup on the filter is expected. Particulate buildup on the filter increases the flow resistance and decreases the flowrate over time, affecting the accuracy of the sample volume determination.

At the conclusion of the sample collection period, the final flow indicator reading is recorded, and the sampler is turned "off". The final elapsed timer reading is then recorded. Wearing clean cotton gloves, the field blank is unpackaged once more and set aside. The sample is now carefully recovered by removing the filter and sorbent cartridge from the sampling module, folding and placing the glass fibre filter into the glass cartridge containing the PUF sorbent, and re-packaging the sample in the original aluminum foil and zip-loc bag. The field blank is recovered and repackaged and a final calibration check is performed using the calibration orifice.

Finally, chain-of-custody records are completed for each sample and the samples are submitted to the analytical laboratory.

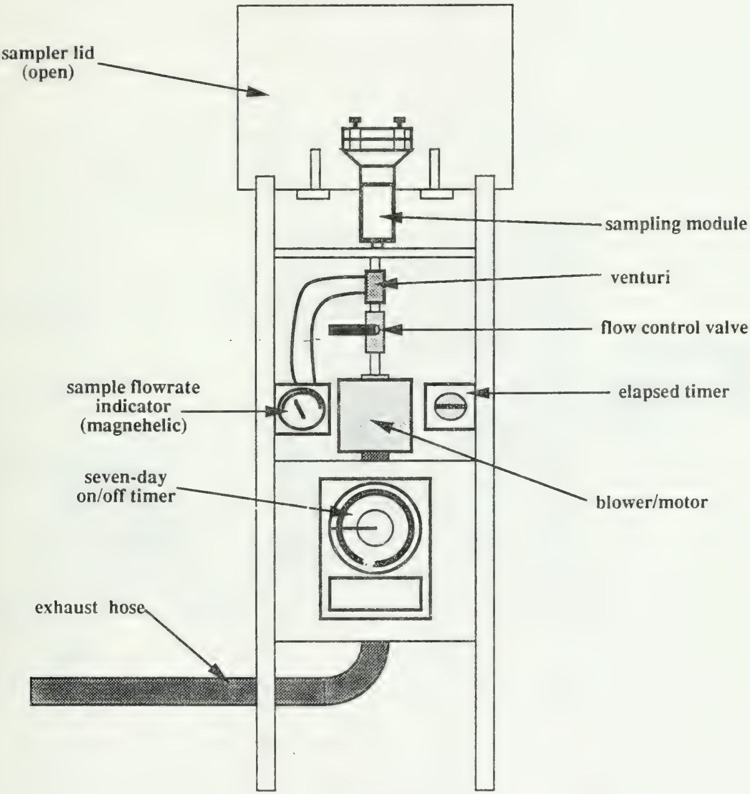

Figure 9: ENSR: GMW PS-1 Sampler Schematic

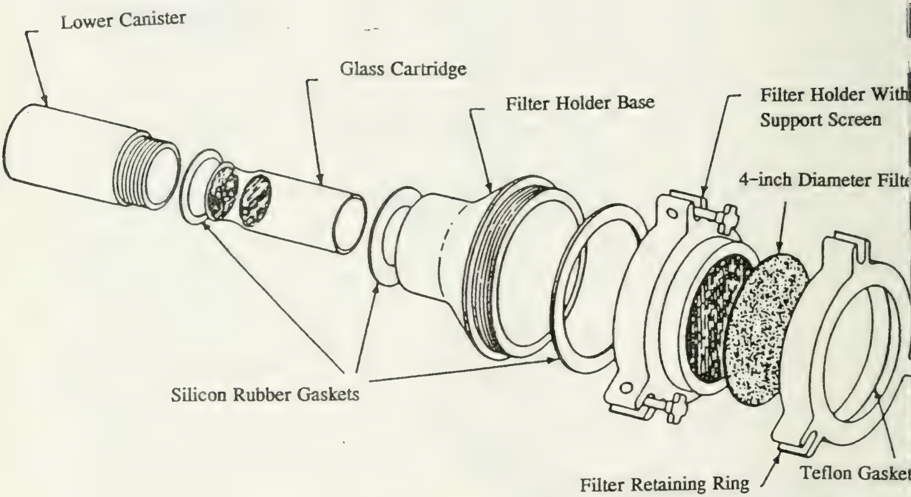

Figure 10: ENSR: Schematic of PS-1 Sampling Module

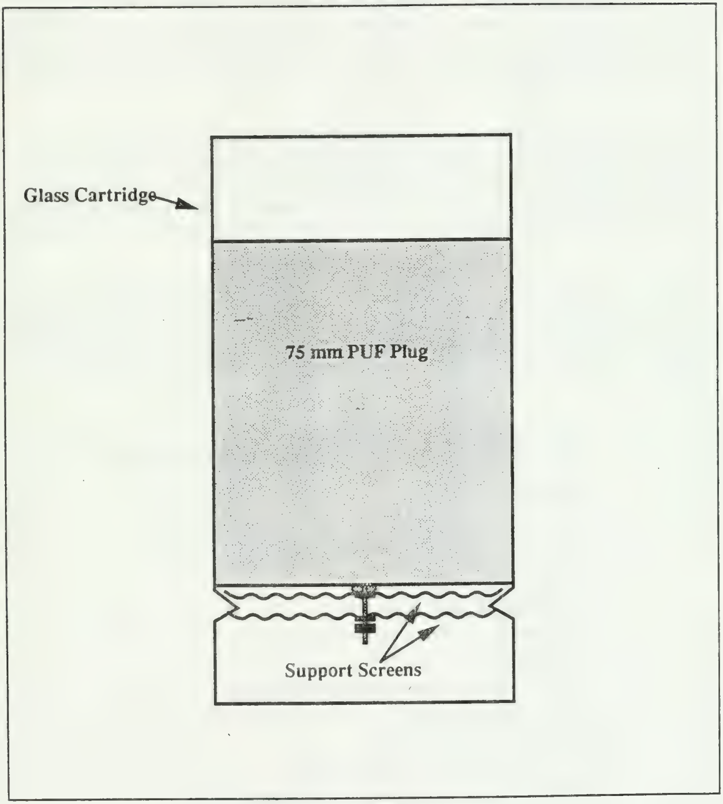

Figure 11: ENSR: PUF Sampling Cartridge

Sampler Siting Requirements

In the collection of ambient air samples for PCDDs/PCDFs, it is important to avoid any possible sample contamination or bias. This means that, in addition to meeting standard siting criteria for TSP sampling, additional criteria must be considered. For example, samplers should not be mounted on platforms or close to utility poles which have been treated with organic wood preservatives as they may contribute to sample contamination and bias. Likewise, samplers should be located away from utility or railroad lines where herbicides have been used in the past.

For short term ambient air monitoring programs, ordinary construction scaffolding make excellent platforms for PS-1 samplers. Typically, this scaffolding can be rented at any equipment rental centre. A section of this scaffolding is usually about 6 feet above the ground, and 4 feet by 8 feet in area. Several platform sections can be carried in the back of a pickup truck and assembled quickly on site. In addition, each section has a built-in ladder for easy access.

In any event, typical siting criteria also includes locating the sampler up off the ground to avoid re-entrainment of dust and soil. The samplers should be located in an open area, at least 2 meters away from any obstruction to air flow. The exhaust hose from the sampler should be extended to its full length, and if possible, in a downwind direction from the sampler.

Table 1. ENSR: Typical Field Operations Sequence of Events

1. Perform Initial Calibration Check
2. Clean and Rinse Sampler Head
3. Load Sorbent Module, Open Field Blank
4. Set "ON-OFF" Timer
5. Record Elapsed Timer Indication
6. Start Sampler, Set and Record Initial Flow, Close Field Blank
7. Record Flow Indication During Sample Run, Verify Sampler Operation
8. Record Final Flow Indication
9. Turn "OFF" Sampler, Open Field Blank, Recover Sample, Record Elapsed Timer Indication
10. Recover Field Blank, Perform Final Calibration Check

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Chapter 3

Sample Analysis Methods

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SUMMARY

Analytical methodology is described which is applicable for the quantitative measurement, using coupled Gas Chromatography-Mass Spectrometry (GC-MS) of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), including both the total chlorinated congener groups (tetra-through octachlorinated) and the 2,3,7,8-chlorine substituted isomers, which are present in ambient air particulates and/or in the vapor phase. Sample extraction and prefractionation or cleanup procedures are discussed, as well as appropriate GC-MS operating parameters. Factors affecting the selection and use of certain capillary GC columns, and the use of high-resolution vs. low-resolution mass spectrometry are reviewed. Typical data obtained in the analyses of actual ambient air samples for PCDD/PCDF, using the methods described, are presented to illustrate the applicability of these procedures. Potential problems which may be encountered in these analyses, and means of resolving these problems are also discussed.

INTRODUCTION

As described in the foregoing Chapters in this volume, the current state-of-the-art for sampling and collection of organic compounds, such as PCDD/PCDF, entails use of a high volume air sampler fitted with a particulate filter, backed up by solid sorbent cartridge containing polyurethane foam plug (PUF), or PUF in combination with other sorbents such as XAD resin. Therefore, two samples are produced for analysis using such an air sampling device, the filter and collected particulates, which may contain sorbed organics, and the sorbent cartridge, which contains trapped organics which were present in the vapor phase in the ambient air sampled. These two types of samples can be analyzed separately if one wishes to obtain insight into the relative distribution of particulate-bound organics as compared to vapor phase organics present in the ambient air, although one must be cautious in ascribing the organics detected in the solid sorbent cartridge solely to vapor phase components. Alternatively, if one is only interested in the total burden of organics collected by the ambient air sampler, then the filter/particulates and

solid sorbents can be combined for analysis as a single sample.

Conceptually, the analytical procedures applied to determine PCDD/PCDF in the filter/particulates and solid sorbents resulting from an ambient air sampling event are the same as those applied to determine these analytes in other types of sample matrices. While these analyses are complex and labor and equipment intensive (and therefore costly), the analytical methodology required is by now well established, and has been described in several previous publications (1-7). The methodology entails four general steps:

1. Extraction of PCDD/PCDF from the filter/particulates and solid sorbent cartridge

2. Separation of PCDD/PCDF from the majority of matrix components and other chemical residues which were extracted from the samples, and concentration of the PCDD/PCDF into a very small volume of solvent

3. Analysis of the fractionated and concentrated extract using GC-MS

4. Assessment of the analytical results to ensure that these data satisfy a defined set of criteria.

Each of these steps will now be discussed in detail.

<u>Analytical Procedures for Quantitative Measurement of PCDD/PCDF in Samples from an Ambient Air Sampler</u>

Extraction of PCDD/PCDF from Filter/Particulates and Solid Sorbent Cartridges Using a Soxhlet Extractor. Extraction of samples from the ambient air sampler is usually accomplished by using a Soxhlet extractor. In the procedures described here, the filter/particulates and solid sorbent are treated as a single sample and are extracted together. The thimble normally used in the Soxhlet extraction chamber to hold samples is not required in this application. If an appropriately sized Soxhlet apparatus is used, the particulate filter and PUF cartridge will fit directly into the extraction chamber. The extraction procedures follow.

- ❑ Prepare a Soxhlet extraction apparatus, consisting of a Soxhlet extraction tube, a 1000 mL single-neck round-bottom flask and a water-cooled condenser, for use, by rinsing it sequentially with methanol, acetone, and methylene chloride, and allowing it to air-dry. Place 600 mL of toluene along with 6 to 10 pre-cleaned 4 mm glass beads, in the round bottom flask. Assemble the entire apparatus, heat the contents of the flask using a heating mantle to reflux temperature, and allow refluxing to continue for a period of about 3 hours.

- ❑ Remove the heating mantle from the Soxhlet flask, allow the apparatus to cool, and then decant the toluene into a clean, 1000 mL flint glass bottle and seal the bottle with a Teflon-lined screw cap. This solution is retained, and periodically

analyzed as a Soxhlet "blank" to check the cleanliness of the apparatus, a QA/QC measure.

- ❑ Place a fresh 600 mL aliquot of toluene into the precleaned Soxhlet flask and re-connect the extraction tube to the flask. Carefully, transfer the glass fiber filter and particulates thereon to the Soxhlet extraction chamber, then place the PUF cartridge (and sorbents if used) on top of the filter in the extraction chamber.

- ❑ Using a microsyringe, add a known quantity, typically, 0.2-5 ng, of an internal standard solution (see section on standards which follows) typically containing $^{13}C_{12}$-2,3,7,8-TCDD, $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-2,3,7,8-TCDF, $^{37}Cl_4$-2,3,7,8-TCDF, $^{13}C_{12}$-1,2,3,7,8-PeCDF, $^{13}C_{12}$-1,2,3,7,8-PeCDD, $^{13}C_{12}$-1,2,3,6,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF, $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD, $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF, $^{13}C_{12}$-OCDD, and $^{13}C_{12}$-OCDF onto the samples in the Soxhlet extraction chamber. Place the condenser on the Soxhlet extraction tube and heat the solvent reservoir so that the extraction solvent refluxes. Continue to extract the sample with the refluxing toluene for a period of 16 hours, then discontinue heating the apparatus and allow it to cool.

- ❑ Transfer the toluene extract to a 1 L concentrating flask, rinsing the extraction reservoir several times with small portions of toluene, and adding these to the extract. Add 1 mL of tridecane to the flask and concentrate the extract to approximately 10 mL by use of a rotary evaporator.

- ❑ Using a 10 mL disposable pipette, transfer the concentrated solution obtained in Step 5 to a pre-rinsed, 125 mL flint glass bottle fitted with a Teflon-lined screw cap, and rinse the rotary evaporator flask four times using 10 mL aliquots of hexane (transferring each rinse solution to the bottle) to effect a quantitative transfer of the concentrate to the bottle.

Separation of PCDD/PCDF from Major Matrix Components and Other Chemical Residues Contained in the Extract

The organic extract obtained utilizing the procedures described in the preceding section is subjected to the fractionation procedures which follow.

1. Add 30 mL of aqueous potassium hydroxide (20% w/v) to the bottle containing the sample extract, seal the bottle and agitate it for a period of 10 minutes. Aspirate and discard the aqueous phase, retaining the organic phase.

2. If the aqueous layer from the previous step appears to be colored following the base extraction procedure, then repeat this operation.

3. Add 30 mL of double-distilled water to the organic phase from Step 1, seal the bottle, and agitate the mixture for a period 1 minute. Again, aspirate and discard the aqueous phase, retaining the organic phase.

4. Add 30 mL of concentrated sulfuric acid to the residual hexane extract from the previous step, seal the bottle, and agitate it for a period of 10 minutes. If emulsions form, centrifuge the bottle to achieve separation of the organic and acidic aqueous phases. Remove and discard the aqueous acidic layer, retaining the organic layer.

5. Repeat the concentrated sulfuric acid wash (the foregoing step), again adding 30 mL of sulfuric acid to the sample extract, and agitating the acidified sample for 10 minutes. Again, aspirate and discard the aqueous layer. Repeat this step until the acid layer is visibly colorless.

6. Repeat Step 3.

7. Add 5 g of anhydrous sodium sulfate to the organic extract and allow the mixture to stand for at least 15 minutes.

8. Quantitatively transfer the organic extract, using hexane to rinse the sample bottle, to a clean test tube, and reduce the volume to approximately 5 mL by passing a stream of pre-purified nitrogen over the extract, while maintaining the test tube at 55oC in a water bath.

9. Fabricate a glass chromatography-column (20 mm OD x 230 mm long) tapered to 6 mm OD on one end. Pack the column, in succession, with a plug of glass wool (silanized), 1.0 g silica, 2.0 g silica containing 28% (w/w) 1 M NaOH, 1.0 g silica, 4.0 g silica containing 30% (w/w) sulfuric acid, and 2.0 g silica.

10. Quantitatively transfer the concentrated extract obtained in Step 8, along with two rinsings of the sample container, using 5 mL portions of hexane each time, to the column and elute the column with 90 mL of hexane. Collect the entire eluate and concentrate to a volume of 1 mL in a centrifuge tube.

11. If any layer of the silica gel column implemented in Step 2 becomes visibly discolored as the column is eluted, repeat Steps 9 and 10.

12. Prepare a liquid chromatography column (11 mm OD x 120 mm) by packing the constricted end with a plug of silanized glass wool and then adding three grams of basic alumina (prepared as described in the following section).

13. Aspirate the concentrated extract obtained in Step 10 and transfer it onto the alumina column prepared in Step 12. Rinse the test tube which contained the concentrate successively with three 1 mL portions of hexane, each time transferring the rinse

solution to the alumina column.

14. Elute the alumina column as follows:

    (a) Elute the column with 15 mL of hexane, taking care not to let the column become completely dry during the elution, and discard the entire eluate.
    (b) Elute the column with 10 mL of 8% (v/v) methylene chloride-in-hexane and discard the entire eluate.

    (c) Elute the column with 15 mL of 50% (v/v) methylene chloride-in-hexane, retaining this entire eluate, and reduce its volume to about 1.0 mL by passing a stream of pre-purified nitrogen over the solution while heating the solution in a 55oC water bath.

15. Prepare a 9.5 x 0.5 cm gravity-flow liquid chromatography column by cutting off a 9-inch disposable Pasteur pipet 1 cm above the constricted tip. Insert a filter disk through the bottom of the column, and position the disk 2.5 cm below the indentation. Through the top of the column, add a sufficient quantity of PX-21 Carbon/Celite 545 (prepared as described in the following section) to form a 2 cm packed bed of the Carbon/Celite. Insert a glass wool plug on top of the Carbon/Celite. Pre-elute the column sequentially with 2 mL of a 50% benzene/50% ethyl acetate solution (v/v), 1 mL of a 50% methylene chloride/50% cyclohexane solution (v/v), and 2 mL of hexane, and discard these eluates. Transfer the collected and concentrated eluate from the alumina column (Step 14) onto the Carbon/Celite column, along with 1 mL of a hexane rinse of the original sample vessel. Elute the column sequentially with 2 mL of 50% methylene chloride/50% cyclohexane solution and 2 mL of 50% benzene/50% ethyl acetate and discard these eluates. Invert the column and elute it (in the reverse direction) with 4 mL of toluene, retaining this entire eluate. Concentrate the collected fraction using a stream of pre-purified nitrogen.

16. Repeat Steps 12 through 14, if preliminary analysis indicates that the extract is still not sufficiently "clean" to yield good GC-MS results.

17. Transfer the 0.5 mL concentrate from Step 15 or 16 into a 3 mL reaction vial. Rinse the tube which contained the concentrate with two 1 mL portions of methylene chloride and transfer these to the reaction vial. By directing a stream of pre-purified nitrogen over the solution in the reaction vial, concentrate the solution to incipient dryness.

18. Seal the sample vessel and store it in a freezer (-15*C). Just prior to GC-MS analysis, remove the vessel from the freezer, allow it to warm to ambient temperature, and reconstitute the residue in the vessel by adding 10 uL of Standard 5023-1 to the vial (see following sections for description of standards).

Reagents and chemicals. Reagents and chemicals used in implementing the procedures described

herein are described in the following.

- Potassium hydroxide, anhydrous; granular sodium sulfate; and sulfuric acid: all Reagent Grade. The granular sodium sulfate is purified prior to use by placing it in a 400oC oven for four hours, then removing it and allowing it to cool in a desiccator. The purified sodium sulfate is stored in a bottle fitted with a Teflon-lined screw cap.

- Acetone, hexane, methylene chloride, benzene, isooctane: "Distilled in Glass" Burdick and Jackson, or equivalent.

- Dodecane and Tridecane: Reagent Grade.

- Basic Alumina (Activity Grade 1): ICN Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600oC in a muffle furnace and then allowing it to cool in a desiccator for 30 minutes prior to use.

- Silica (Bio-Sil A 100/200 mesh): Bio-Rad. The Bio-Sil A is conditioned prior to use by combining 90 g of this sorbent (as received) with 10 g of water in a screw-capped glass bottle fitted with a Teflon-lined cap. The bottle is sealed and agitated to disperse any aggregates and the deactivated silica is stored in the bottle in a desiccator.

- Silica Gel Impregnated with Sulfuric Acid (30% w/w): Concentrated sulfuric acid (4.4 g) is combined with 10.0 g silica gel (prepared as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H2SO4-silica gel is stored in the capped bottle (fitted with a Teflon-lined cap).

- Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (30 g) is combined with 100 g Bio-Sil A (prepared as described above) in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in the capped bottle (fitted with a Teflon-lined cap).

- Carbon/Celite: A 10.7 g aliquot of PX-21 carbon (Anderson Development Co., Adrian, Michigan) is combined with 125 g of Celite 545 (Supelco, Inc.) in a 250 mL glass bottle, fitted with a Teflon-lined cap, and the mixture is agitated to obtain a uniform mixture. The Carbon/Celite mixture is stored in the capped bottle.

- Nitrogen: Pre-purified Grade; and Hydrogen: Ultra High Purity.

Calibration and spiking standards. PCDD and PCDF standards which are required for the

analyses described herein must either be purchased as prepared solutions from reliable suppliers (Wellington Scientific, Cambridge Isotope Laboratories), or must be prepared by the analyzing laboratory. In the latter case, stock standard solutions of various PCDD and PCDF isomers and mixtures thereof are prepared by weighing and diluting appropriate quantities of the authentic isomers. The stock solutions are contained in appropriate amber bottles and are stored tightly capped in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These stock standards are checked regularly to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. Some typical standard solutions used in our laboratory are listed below,

1. **Standard Mixture 5001-12.**
   Prepare a stock solution containing the following isotopically-labelled CDD and CDF in tridecane at the indicated concentrations: 50 pg/uL $^{13}C_{12}$-2,3,7,8-TCDD; 20 pg/uL $^{37}C_{14}$-2,3,7,8-TCDD; 50 pg/uL $^{13}C_{12}$-2,3,7,8-TCDF; 20 pg/uL $^{37}Cl_4$-2,3,7,8-TCDF; 50 pg/uL $^{13}C_{12}$-1,2,3,7,8-PeCDD; 50 pg/uL $^{13}C_{12}$-1,2,3,7,8-PeCDF; 125 pg/uL $^{13}C_{12}$-1,2,3,6,7,8-HxCDD; 125 pg/uL $^{13}C_{12}$-1,2,3,4,7,8-HxCDF; 125 pg/uL $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD; 125 pg/uL $^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF; 250 pg/uL $^{13}C_{12}$-OCDD; and 250 pg/uL $^{13}C_{12}$-OCDF. Portions of this isomer mixture are added to all samples prior to analyses, the $^{13}C_{12}$-labelled PCDD isomers serving as internal standards for use in quantitation of the native PCDD and the $^{13}C_{12}$-labelled PCDF isomers serving as internal standards for use in quantitation of the native PCDF isomers. The $^{37}Cl_4$-2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDF are used as surrogates, and the recoveries of these surrogates, as well as the recoveries of the other internal standards, are used to gauge the overall efficacy of the analytical procedures.

2. **Standard 5023-1.**
   Prepare a stock solution containing 0.05 ng/uL of $^{13}C_{12}$-1,2,3,4-TCDD and 0.1 ng/uL of $^{37}Cl_4$-1,2,7,8-TCDF in tridecane. This standard mixture is used to reliably estimate the recovery of the TCDD and TCDF internal standards.

3. **Standard Mixture 5001-10.**
   Prepare a stock solution of the following CDD and CDF isomers in isooctane at the indicated concentrations: 50 pg/uL 2,3,7,8-TCDD; 50 pg/uL 2,3,7,8-TCDF; 50 pg/uL 1,2,3,7,8-PeCDD; 50 pg/uL 1,2,3,7,8-PeCDF; 50 pg/uL 2,3,4,7,8-PeCDF; 125 pg/uL 1,2,3,6,7,8-HxCDD; 125 pg/uL 1,2,3,7,8,9-HxCDD; 125 pg/uL 1,2,3,4,7,8-HxCDD; 125 pg/uL 1,2,3,4,7,8-HxCDF; 125 pg/uL 2,3,4,6,7,8-HxCDF; 125 pg/uL 1,2,3,6,7,8-HxCDF; 125 pg/uL 1,2,3,7,8,9-HxCDF; 125 pg/uL 1,2,3,4,6,7,8-HpCDD; 125 pg/uL 1,2,3,4,6,7,8-HpCDF; 100 pg/uL 1,2,3,4,7,8,9-HpCDF; 250 pg/uL OCDD; and 250 pg/uL OCDF. This mixture of all the 2,3,7,8-chlorine-substituted CDD and CDF is used to determine GC-MS response factors for these isomers, and also to define GC retention

times for these isomers on the several capillary GC columns used in the analysis. This mixture is also used to spike selected samples from a given batch, which are then analyzed. The recoveries of the native isomers which are achieved provide a measure of the efficacy of the overall analytical methodology for determining these isomers.

4. **Standard Mixtures 5001-1 through 5001-9.**
Prepare stock solutions of the working standards consisting of mixtures of all of the native 2,3,7,8-chlorine substituted CDD and CDF isomers, as well as selected $^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted CDD/CDF isomers (including one $^{13}C_{12}$-labelled isomer of each chlorinated congener group) in the concentrations indicated in Table 1. These are the same isomers as those included in Standard Mixtures 5001-14 and 5001-10.

5. **Standard Mixture BL-M005.**
This standard contains the first-eluting and last-eluting isomers for each chlorinated class (tetra- through octachlorinated) of PCDD, as well as the TCDD isomers which elute closest to 2,3,7,8-TCDD on the 60 M DB-5 column. These latter isomers are included in the calibration standard for the purpose of verifying each day that the DB-5 column in use separates the 2,3,7,8-TCDD isomer from all other TCDD isomers. This standard contains 50 pg/uL of each of 2,3,7,8-TCDD; 1,3,6,8-TCDD; 1,3,7,9-TCDD; 1,2,3,7-/1,2,3,8-TCDD; 1,2,3,9-TCDD; 1,2,3,4,-TCDD; 1,2,8,9-TCDD; 1,2,4,6,8-/1,2,4,7,9-PeCDD; 1,2,3,8,9-PeCDD; 1,2,4,6,7,9-/1,2,4,6,8,9-HxCDD; 1,2,3,4,6,7-HxCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDD and OCDD.

6. **Standard Mixture BL-M006.**
This standard contains the first-eluting and last-eluting isomers (when the 60 M DB-5 column is employed) for each chlorinated class (tetra-through octachlorinated) of CDF. The calibration solution contains 50 pg/uL of each of 1,3,6,8-TCDF; 1,2,8,9-TCDF; 1,3,4,6,8-PeCDF; 1,2,3,8,9-PeCDF; 1,2,3,4,6,8-HxCDF; 1,2,3,4,8,9-HxCDF; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; and OCDF.

7. **Standard Mixture 5014-1.**
Prepare a solution containing approximately 0.10 ng/uL 2,3,7,8-TCDD; 0.10 ng/uL 2,3,7,8-TCDF; 0.025 ng/uL $^{13}C_{12}$-2,3,7,8-TCDD; 0.01 ng/uL $^{37}Cl_4$-2,3,7,8-TCDD; 0.01 ng/uL $^{37}Cl_4$-2,3,7,8-TCDF; 0.025 ng/uL $^{13}C_{12}$-2,3,7,8-TCDF; 0.025 ng/uL $^{13}C_{12}$-1,2,3,4-TCDD; 0.05 ng/uL of each TCDD isomer other than 2,3,7,8-TCDD (21 other TCDDs) and 0.05 ng/uL of each TCDF isomer other than 2,3,7,8-TCDF (37 other TCDFs). This standard is used to determine the efficacy of a particular gas chromatographic column, such as the DB-DIOXIN column, for separating 2,3,7,8-TCDD from the other TCDD isomers, and 2,3,7,8-TCDF from the other TCDF isomers. This standard is also used to determine the relative retention times of the TCDD and TCDF isomers.

Gas Chromatographic-Mass Spectrometric Procedures for Quantitating PCDD/PCDF in Ambient Air Sample Extracts

Ambient air sample extracts prepared by the procedures described in the previous section are quantitatively analyzed for PCDD/PCDF using GC-MS. Prior to discussing the detailed procedures, some general considerations regarding choice of GC columns and mass spectrometric instrumentation for these analyses are presented.

Selection of GC columns for PCDD/PCDF analyses. Capillary GC columns are required for these analyses since they yield superior chromatographic resolution of PCDD/PCDF isomers and permit detection of very small quantities of these compounds (as low as a few femtograms). A 60M DB-5 capillary GC column completely resolves each of the tetra-, penta-, hexa-, hepta- and octachlorinated congener groups of the PCDD and PCDF, and therefore directly yields accurate data for these total chlorinated congener groups. In addition, as shown in Table 2, the DB-5 column yields isomer-specific data for all seven of the 2,3,7,8-substituted PCDD isomers and for three of the 2,3,7,8-substituted PCDF isomers. The remaining seven 2,3,7,8-substituted PCDF isomers, including 2,3,7,8-TCDF, are not uniquely resolved on the DB-5 column and coelute with other PCDF. However, 2,3,7,8-TCDF and five other PCDF isomers not resolved on DB-5 can be uniquely resolved by using the new DB-DIOXIN capillary GC column, which was developed by Wright State University and J & W Scientific (see Table 2). Therefore, following the initial analysis of the ambient air sample eluate on the DB-5 column, another aliquot of the same sample is analyzed using a 60M DB-DIOXIN capillary GC column. Even when both of the capillary GC columns just described are utilized, one of the 2,3,7,8-substituted PCDF isomers, 1,2,3,4,7,8-HxCDF, is not uniquely resolved.

Choice of mass spectrometric instrumentation for PCDD/PCDF analyses-high-resolution MS vs. low-resolution MS. The choice between high- and low-resolution MS for the PCDD/PCDF analyses described herein is dictated by the requirements and objectives of a particular ambient air sampling project. Here, "high" resolution is typically 1:10,000 while "low" resolution is typically 1:3000 for a sector type mass spectrometer operated at low resolution and 1:500 for a low-resolution quadrupole mass spectrometer. The achievement of optimum specificity in the analyses, of course, requires the use of high-resolution MS. Even with the extensive sample extract cleanup procedures described earlier, and in spite of the use of very high resolution capillary GC columns, in some cases, compounds other than PCDD/PCDF may be present in the sample extracts which give responses at the same nominal ion masses as the PCDD/PCDF of interest, and which are not mass spectrometrically resolved at lower mass resolution. In these cases, the indicator molecular ion ratios (discussion of these follows) are usually outside the acceptable ranges which are specified for PCDD/PCDF. In such instances, high resolution mass spectrometry will sometimes (but not always) resolve the interfering component. Another factor affecting the choice between high- and low-resolution mass spectrometry for PCDD/PCDF analyses is the sensitivity required. The best currently available high-resolution MS instruments can typically detect and measure, with adequate signal-to-noise, 10-50 femtograms of PCDD/PCDF isomers when operated in the selected ion-monitoring, electron-impact mode at a resolution of 10,000. In comparison, a

good sector MS operated at low resolution (typically, 1:3000 resolution) in the same mode can detect 1-2 picograms of PCDD/PCDF, whereas a quadrupole MS, (typical resolution of 1:300 to 1:500) can typically detect no lower than 20-50 pg of PCDD/PCDF. On the other hand, sample throughput may be somewhat greater for a low-resolution MS than for a high-resolution MS, and the cost of the latter instrumentation is substantially greater than that of a low-resolution instrument.

It should be emphasized that, irrespective of whether high- or low-resolution MS is utilized for PCDD/PCDF analyses, full-scale cleanup of sample extracts (using all of the procedures described earlier) prior to GC-MS is essential to good performance. Failure to adequately cleanup extracts subjected to GC-MS can result in rapid degradation or failure of expensive capillary GC columns; substantial increases in the time required between successive injections of samples owing to compounds in the extract having long retention times (with a resultant reduction in sample throughput); shifts in observed GC retention times and/or distortion of GC peak shapes for PCDD/PCDF analytes, owing to excessive extract constituents which overload the GC column; and more rapid degradation of MS performance due to deposition of extract constituents onto MS ion source and analyzer parts.

GC-MS instrumentation and operating parameters. Specific GC-MS instrumentation and operating parameters which are used by Wright State for GC-high resolution MS analyses of ambient air extracts and other samples for PCDD/PCDF are listed below. Other equivalent instrumentation may also be used for these analyses, of course.

1. **Gas Chromatograph: Carlo Erba Mega 5000**

   a. Injector: Configured for capillary column, splitless/split injection; injector temperature, 280°C.

   b. Capillary GC Columns and Carrier Gas:

      ✓ For DB-5 column (J & W Scientific, 60M, 0.25 mm. I.D., 0.25 um film): Helium carrier gas, 40 lb. head pressure, direct coupled to MS.

      ✓ For DB-DIOXIN column (J & W Scientific, 60M, 0.25 mm. I.D., 0.25 um film): Helium, 40 lb. head pressure, direct coupled to MS.

Table 1: Calibration Standards
Concentrations in Calibration Solutions in pg/μL Tridecane

Calibration Standard WSU Lot Number	CS1 5001-1	CS1 5001-2	CS2 5001-3	CS3 5001-4	CS4 5001-5	CS5 5001-6	CS6 5001-7	CS7 5001-8	CS8 5001-9
2,3,7,8-TCDD	2000	200	100	50	25	10	5	2.5	1
2,3,7,8-TCDF	2000	200	100	50	25	10	5	2.5	1
1.2.3.7.8-PeCDD	2000	200	100	50	25	10	5	2.5	1
1,2,3,7,8-PeCDF	2000	200	100	50	25	10	5	2.5	1
2,3,4,7,8-PeCDF	2000	200	100	50	25	10	5	2.5	1
1,2,3,4,7,8-HxCDD	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,7,8-HxCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,7,8,9-HxCDD	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,7,8-HxCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,6,7,8-HxCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,7,8,9-HxCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
2,3,4,6,7,8-HxCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,6,7,8-HpCDD	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,6,7,8-HpCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,7,8,9-HpCDF	5000	500	250	125	62.5	25	12.5	6.25	2.5
OCDD	10,000	1000	500	250	125	50	25	12.5	5
OCDF	10,000	1000	500	250	125	50	25	12.5	5
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	50	50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	50	50	50	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	125	125	125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	125	125	125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	125	125	125	125	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	125	125	125	125	125	125	125	125	125
$^{13}C_{12}$-OCDD	250	250	250	250	250	250	250	250	250
$^{13}C_{12}$-OCDF	250	250	250	250	250	250	250	250	250
$^{37}Cl_4$-2,3,7,8-TCDD	20	20	20	20	20	20	20	20	20
$^{37}Cl_4$-2,3,7,8-TCDF	20	20	20	20	20	20	20	20	20
$^{13}C_{12}$-1,2,3,4-TCDD	50	50	50	50	50	50	50	50	50

Table 2: Capillary Columns on which the 2,3,7,8-Substituted PCDD/PCDF Isomers are Separated From Other PCDD/PCDF Isomers

PCDD/PCDF ISOMERS	DB-5[a]	DB-DIOXIN[a]
2378-TCDD	X	X
12378-PeCDD	X	-
123478-HxCDD	X	-
123678-HxCDD	X	X
123789-HxCDD	X	X
1234678-HpCDD	X	X
OCDD	X	X
2378-TCDF	-	X
12378-PeCDF	-	X
23478-PeCDF	-	X
123478-HxCDF[b]	-	-
123678HxCDF	-	X
123789-HxCDF	-	X
234678-HxCDF	-	X
1234678-HpCDF	X	X
1234789-HxCDF	X	X
OCDF	X	X

a. X= Isomer resolved; - = Isomer coelutes with other isomers
b. Not specific on any column

c. Temperature Program for DB-5 Column: See Table 3. Temperature Program for DB-DIOXIN Column: See Table 4.

d. Interface Temperature: 250°C

2. **Mass Spectrometer: Kratos MS-890**

a. Ionization Mode: Electron impact (70 eV)

b. Static Resolution: 1:10,000 (10% valley) or higher

c. Source Temperature: 250°C

d. Accelerating Voltage: 6KV

e. Ions Monitored: Computer controlled Selected Ion Monitoring is employed. Tables 3 and 4 list the ion masses which are indicators of PCDD/PCDF of each chlorinated congener group and the time intervals during these ions are monitored. These tables also show the expected [M]+/[M+2]+ ratios for ion responses arising from PCDD/PCDF. Note that appropriate chlorinated diphenylether molecular ions. are also monitored, as indicated in Tables 3 and 4.

GC and MS calibration procedures. Calibration procedures which are necessary to ensure the quality and reliability of the GC-MS data obtained in the analyses are summarized below.

- ❑ Calibrating the MS Mass Scale: Perfluorokerosene is introduced into the MS in order to calibrate the mass scale through at least m/z 515. The mass calibration is rechecked at least once during each 8 hr. operating period.

- ❑ Table 3 shows a typical GC temperature program for the 60 M DB-5 column which is utilized to resolve each chlorinated class of PCDD and PCDF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the MS. Table 4 shows corresponding information for the DB-DIOXIN columns. The temperature programs and ion monitoring time cycles must be established for each column prior to accomplishing the analyses by using appropriate PCDD and PCDF standards and GC window-defining solutions (BL-M005, BL-M006, BL-M007, and BL-M008, described earlier).

- ❑ Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Standard

Mixture 5014-1 is used to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, respectively, on the capillary GC column used. A 25% valley (or less) must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers, and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs is required. Standard Mixture 5014-1 is utilized with the DB-5 column according to the conditions specified above and in Table 3. This standard mixture is also utilized with the DB-DIOXIN column. The column performance evaluation must be accomplished each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. When the same column is employed for a period of time, its performance is also gauged by noting the peak width (at one-half peak height) for 2,3,7,8-TCDD and for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory operation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new GC column must be installed.

- ❑ Calibration of the GC-MS-DS system to accomplish quantitative analyses of total PCDD and PCDF by chlorinated congener group, and of each of the 2,3,7,8-substituted PCDD and PCDF isomers contained in the sample extract is typically accomplished by analyzing a series of nine working calibration standards. Each of these standards is prepared to contain the same concentration of each of the appropriate stable-isotopically labelled internal standards used here but a different concentration of the appropriate native PCDD/PCDF. Mixtures are typically prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD/PCDF falls within the range of 0.02 to 40.0 in the nine working calibration mixtures. The external standard described in an earlier section is added to the sample vial prior to GC-MS analysis of the calibration standard and is employed to determine the percent recovery for each of the 13C12-labeled internal standards.

Calculation of response factors, concentrations of PCDD/PCDF, and recoveries of internal standards. The equations employed for calculating response factors from GC-MS calibration data, for determining the concentrations of native PCDD/PCDF in the sample analyzed, and for calculating recoveries of the internal standards are exemplified by those shown below. The examples given are the equations used for 2,3,7,8-TCDD, but these can be generalized to any particular PCDD/PCDF isomer (or GC-MS peak response) by inserting the appropriate data for the isomer of interest and for the $^{13}C_{12}$-PCDD or $^{13}C_{12}$-PCDF internal standard which is the reference for that isomer.

Table 3: Sequence of Operation in GC-MS-DS Quantitation of PCDD/PCDF in Extracts of Ambient Air Samples Using a DB-5 Column

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temp.Prog. Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approx. Theor. Ratio[b]
0	Injection, splitless	180					
1	Turn on split valve	180					
1	Begin temp. program to 300°C	180	15				
2	Close split valve	195	(up to 220°C)				
16	Start Tetra Program;			240.9378	[M-COCl]+	TCDF	
	time/mass=0.08 sec.	220		256.9328	[M-COCl]+	TCDD	
				303.9016	[M]+	TCDF	0.77
				305.8987	[M+2]+	TCDF	
				311.8896	[M]+	$^{37}Cl_4$-TCDF	
				315.9419	[M]+	$^{13}C_{12}$-TCDF	0.77
				317.9389	[M+2]+	$^{13}C_{12}$-TCDF	
				319.8965	[M]+	TCDD	0.77
				321.8936	[M+2]+	TCDD	
				327.8845	[M]+	$^{37}Cl_4$-TCDD	
				331.9368	[M]+	$^{13}C_{12}$-TCDD	0.77
				333.9339	[M+2]+	$^{13}C_{12}$-TCDD	
				373.8393	[M]+	HxDPE[a]	
29	Stop Tetra Program	220					
29	Start Penta Program;			274.8989	[M-C0C1]+	PeCDF	
	time/mass=0.08 sec.	220	3.5	290.8938	[M-C0C1]+	PeCDD	
			(up to 300°C)	337.8626	[M]+	PeCDF	0.62
				339.8597	[M+2]+	PeCDF	
				349.9028	[M]+	$^{13}C_{12}$-PeCDF	0.62
				351.9000	[M+2]+	$^{13}C_{12}$-PeCDF	
				353.8575	[M]+	PeCDD	0.62
				355.8546	[M+2]+	PeCDD	
				365.8977	[M]+	$^{13}C_{12}$-PeCDD	0.62
				367.8949	[M+2]+	$^{13}C_{12}$-PeCDD	
				407.8003	[M]+	HpDPE[a]	
34	Stop Penta Program						
34	Start Hexa Program	238		310.8569	[M+2-COCl]+	HxCDF	
	time/mass = 0.08 sec.			326.8518	[M+2-COCl]+	HxCDD	
				373.8208	[M+2]+	HxCDF	1.23
				375.8178	[M+4]+	HxCDF	
				385.8610	[M+2]+	$^{13}C_{12}$-HxCDF	1.23
				387.8579	[M+4]+	$^{13}C_{12}$-HxCDF	
				389.8157	[M+2]+	HxCDD	1.23
				391.8127	[M+4]+	HxCDD	
				401.8559	[M+2]+	$^{13}C_{12}$-HxCDD	1.23
				403.8529	[M+4]+	$^{13}C_{12}$-HxCDD	
				443.7584	[M+2]+	ODPE[a]	

Table 3 (Continued): Sequence of Operation in GC-MS-DS Quantitation of PCDD/PCDF in Extracts of Ambient Air Samples Using a DB-5 Column

Elapsed Time (min)	Event	GC Column Temperature (°C)	Temp.Prog Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approx. Theor. Ratio[a]
40	Stop Hexa Program	259					
40	Start Hepta Program; time/mass=0.08 sec.	259		344.8179	[M+2-COCl]+	HpCDF	
				360.8128	[M+2-COCl]+	HpCDD	
				407.7818	[M+2]+	HpCDF	1.03
				409.7789	[M+4]+	HpCDF	
				419.8220	[M+2]+	$^{13}C_{12}$-HpCDF	1.03
				421.8189	[M+4]+	$^{13}C_{12}$-HpCDF	
				423.7766	[M+2]+	HpCDD	1.03
				425.7737	[M+4]+	HpCDD	
				435.8169	[M+2]+	$^{13}C_{12}$-HpCDD	1.03
				437.8140	[M+4]+	$^{13}C_{12}$-HpCDD	
				477.7194	[M+2]+	NDPE[a]	
48	Stop Hepta Program	287					
48	Start Oct Program; time/mass=0.08 sec.	287		378.7789	[M+2-COCl]+	OCDF	
				394.7739	[M+2-COCl]+	OCDD	
				441.7428	[M+2]+	OCDF	0.88
				443.7399	[M+4]+	OCDF	
				457.7377	[M+2]+	OCDD	0.88
				459.7348	[M+4]+	OCDD	
				469.7779	[M+2]+	$^{13}C_{12}$-OCDD	0.88
				471.7750	[M+4]+	$^{13}C_{12}$-OCDD	
				511.6804	[M+2]+	DDPE[a]	
54	Stop Octa Program						
61	Column Temp. Hold						
76	Cool Column to 180°C						

b. Approximate Theoretical Ratio: First Mass Fragment Monitored/First Mass + 2 Fragment Monitored

Table 4: Sequence of Operation in GC-MS-DS Quantitation of PCDD/PCDF in Extracts of Ambient Air Samples Using a DB-DIOXIN Column

Elapsed Time (min)	Event	GC Column Temp.(°C)	Temp.Prog. Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approx. Theor. Ratio
0	Injection, splitless	180					
1	Turn on split valve	180					
1	Begin temp.program to 300°C	180	15				
2	Close split valve	195	(up to 220°C)				
16	Start Tetra Program;			240.9378	[M-COCl]+	TCDF	
	time/mass=0.08 sec.	220		256.9328	[M-COCl]+	TCDD	
				303.9016	[M]+	TCDF	0.77
				305.8987	[M+2]+	TCDF	
				311.8896	[M]+	$^{37}Cl_4$-TCDF	
				315.9419	[M]+	$^{13}C_{12}$-TCDF	0.77
				317.9389	[M+2]+	$^{13}C_{12}$-TCDF	
				319.8965	[M]+	TCDD	0.77
				321.8936	[M+2]+	TCDD	
				327.8845	[M]+	$^{37}Cl_4$-TCDD	
				331.9368	[M]+	$^{13}C_{12}$-TCDD	0.77
				333.9339	[M+2]+	$^{13}C_{12}$-TCDD	
				373.8393	[M]+	HxDPE[a]	
27	Stop Tetra Program	220					
27	Start Penta Program;			274.8989	[M-COCl]+	PeCDF	
	time/mass=0.08 sec.	220	3.5	290.8938	[M-COCl]+	PeCDD	
			(up to 270°C)	337.8626	[M]+	PeCDF	0.62
				339.8597	[M+2]+	PeCDF	
				349.9028	[M]+	$^{13}C_{12}$-PeCDF	0.62
				351.9000	[M+2]+	$^{13}C_{12}$-PeCDF	
				353.8575	[M]+	PeCDD	0.62
				355.8546	[M+2]+	PeCDD	
				365.8977	[M]+	$^{13}C_{12}$-PeCDD	0.62
				367.8949	[M+2]+	$^{13}C_{12}$-PeCDD	
				407.8003	[M]+	HpDPE[a]	
33	Stop Penta Program						
33	Start Hexa Program:	241		310.8569	[M+2-COCl]+	HxCDF	
	time/mass = 0.08 sec.			326.8518	[M+2-COCl]+	HxCDD	
				373.8208	[M+2]+	HxCDF	1.23
				375.8178	[M+4]+	HxCDF	
				385.8610	[M+2]+	$^{13}C_{12}$-HxCDF	1.23
				387.8579	[M+4]+	$^{13}C_{12}$-HxCDF	
				389.8157	[M+2]+	HxCDD	1.23
				391.8127	[M+4]+	HxCDD	
				401.8559	[M+2]+	$^{13}C_{12}$-HxCDD	1.23
				403.8529	[M+4]+	$^{13}C_{12}$-HxCDD	
				443.7584	[M+2]+	ODPE[a]	

Table 4 (continued): Sequence of Operation in GC-MS-DS Quantitation of PCDD/PCDF in Extracts of Ambient Air Samples Using a DB-DIOXIN Column

Elapsed Time (min)	Event	GC Column Temp.(°C)	Temp.Prog. Rate (°C/min)	Ions Monitored by Mass Spectrometer (m/z)	Identity of Fragment Ion	Compounds Monitored	Approx. Theor. Ratio
43	Stop Hexa Program	270					
43	Start Hepta Program; time/mass = 0.08 sec.	270		344.8179	[M+2-COCl]+	HpCDF	
				360.8128	[M+2-COCl]+	HpCDD	
				407.7818	[M+2]+	HpCDF	1.03
				409.7789	[M+4]+	HpCDF	
				419.8220	[M+2]+	$^{13}C_{12}$-HpCDF	1.03
				421.8189	[M+4]+	$^{13}C_{12}$-HpCDF	
				423.7766	[M+2]+	HpCDD	1.03
				425.7737	[M+4]+	HpCDD	
				435.8169	[M+2]+	$^{13}C_{12}$-HpCDD	1.03
				437.8140	[M+4]+	$^{13}C_{12}$-HpCDD	
				477.7194	[M+2]+	NDPE[a]	
48	Stop Hepta Program	270					
48	Start Octa Program; time/mass = 0.08 sec.	270		378.7789	[M+2-COCl]+	OCDF	
				394.7739	[M+2-COCl]+	OCDD	
				441.7428	[M+2]+	OCDF	0.88
				443.7339	[M+4]+	OCDF	
				457.7377	[M+2]+	OCDD	0.88
				459.7346	[M+4]+	OCDD	
				469.7779	[M+2]+	$^{13}C_{12}$-OCDD	0.88
				471.7750	[M+4]+	$^{13}C_{12}$-OCDD	
				511.6804	[M+2]+	DDPE[a]	
58	Stop Octa Program	270					
63	Column Temperature Hold	270					
76	Cool Column to 180°						

b. Approximate Theoretical Ratio: First Mass Fragment Monitored/First Mass + 2 Fragment Monitored

a. HxDPE, HpDPE, ODPE, NDPE, DDPE are abbreviations which designate (respectively) hexachloro-, heptachloro-, octachloro-, nonachloro-, and decachlorodiphenyl ethers.

a. Equation 1: Response Factor (RRFa) for native, 2,3,7,8-TCDD Using $^{13}C_{12}$-2,3,7,8-TCDD as an internal standard.

RRFa = (AsCis/AisCs)

where: As = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

Ais = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

Cis = Concentration of the internal standard (pg./uL.)

Cs = Concentration of the 2,3,7,8-TCDD (pg./uL.)

b. Equation 2: Response Factor (RRFb) $^{13}C_{12}$-1,2,3,4-TCDD, the co-injected external standard.

RRFb = (AisCes/AesCis)

where: Ais = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

Aes = SIM response for $^{13}C_{12}$-1,2,3,4-TCDD external standard at m/z 332 + 334

Cis = Concentration of the $^{13}C_{12}$-2,3,7,8-TCDD internal standard (pg/uL)

Ces = Concentration of the $^{13}C_{12}$-1,2,3,4-TCDD external standard (pg/uL)

c. Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using $^{13}C_{12}$-2,3,7,8-TCDD as internal standard.

Concentration, pg./g. = (As) (Is)/(Ais)(RRFa)(W)

where: As = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

Ais = SIM response for the $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

Is = Amount of internal standard added to each sample (pg)

W = Weight of sample in grams

RRFa = Relative response factor from Equation 1

d. Equation 4: Calculation of % recovery of $^{13}C_{12}$-2,3,7,8-TCDD internal standard

% Recovery = 100(Ais)(Es)/(Aes)(Ii)(RRFb)

Ais = SIM response for $^{13}C_{12}$-2,3,7,8-TCDD internal standard ion at m/z 332 + 334

Aes = SIM response for $^{13}C_{12}$-1,2,3,4-TCDD external standard ion at m/z 332 + 334

Es = Amount of $^{13}C_{12}$-1,2,3,4-TCDD external standard co-injected with sample extract (pg)

Ii = Theoretical amount of $^{13}C_{12}$-2,3,7,8-TCDD internal standard in injection (pg)

RRFb = Relative response factor from Equation 2

To calculate the total PCDD and PCDF by congener group or class (that is, total tetra-, total penta-, total hexa-, total hepta-, octa-CDD and octa-CDF), all of the mass chromatographic peaks detected within each congener-group GC window which are identified as components of that group (using the specified criteria shown below) are summed, and a composite response factor is used for the group to derive quantitative data. The latter for a given group is the average of the response factors measured for each isomer of that group which is included in the calibration standards.

Criteria for Qualitative Identification of PCDD/PCDF

In order to assert that GC-MS data obtained in the analyses of ambient air sample extracts are indicative of the presence of PCDD/PCDF, the data must satisfy the following criteria:

- ❑ Mass Spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Tables 3 and 4), and intensities of these ions must maximize at the same retention time, within + 1 second. In addition, the chromatographic retention time observed for each native PCDD/PCDF signal must be the same as that for the corresponding stable-isotopically labeled internal standard.

- ❑ The ratios of the intensity of the molecular ion [M]+ signal to that of the [M+2]+ signal must be within +20% of the theoretically expected ratio for

each class of PCDD/PCDF for which peaks are detected. For example, 0.77 is the theoretical [M]+/[M+2]+ ratio in the case of TCDD; therefore, the acceptable observed range for this ratio in the data is 0.65 to 0.89. (See Tables 3 and 4 for the expected ratios for other PCDD/PCDF groups.)

An ion signal is considered to be detectable if its intensity exceeds that of the baseline noise by a factor of at least 2.5:1.

- ❑ For reliable detection and quantitation of PCDF it is also necessary to monitor signals arising from chlorinated diphenyl ethers which, if present, could give rise to fragment ions yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Tables 3 and 4, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time as the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

- ❑ Occasionally, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (organic compounds present in the sample in high concentrations which are not completely removed during cleanup of the extract) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extraneous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. Such shifts in chromatographic retention times may be compensated to some extent by the analyst's intervention in the GC-MS operating sequence. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe, additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

Problems Commonly Encountered in Analyses of Ambient Air and Other Samples for PCDD/PCDF and Actions to Mitigate These

In analyzing any type of environmental sample, including ambient air, to determine the content of PCDD/PCDF, the analyst is hampered by the fact that such samples typically contain widely varying concentrations of these compounds, as well as of matrix components and other interfering chemical residues. The latter must be removed from the sample extract by the cleanup procedures and the GC separation procedures which were described earlier. However, these procedures have a fixed capacity consistent with the size and quantity of sorbent used in the liquid chromatography columns, as well as the type and dimensions of the GC column used in the analyses. If the quantities of matrix constituents and/or chemical residues other than

PCDD/PCDF which are present in the sample extract exceed the capacities of the cleanup methods (or if the cleanup methods are entirely ineffective for removing such materials), then the analysis may fail. There are several possible indicators of such failures which may be observed, and these indicators and actions which can sometimes be taken to salvage the analyses when these occur are described in the following.

Distortion of the Mass Chromatogram - Poor Mass Chromatographic Peak Shape, Overlap and Smearing of Peaks, Continuously Rising Base Lines

These observations are usually indicators of the presence of excessive quantities of extraneous matrix components or other chemical residues in the sample extract, which in turn are frequently due to overloaded liquid and/or gas chromatographic columns. The presence of extraneous interferences in the processed sample extract subjected to GC-MS analysis is also sometimes indicated by apparent recoveries of the isotopically-labeled PCDD/PCDF internal standards which exceed 100%. In such cases, rechromatographing the remaining sample extract by subjecting it to one or more additional liquid chromatography cleanup sequences, especially the alumina column cleanup, prior to repeating the GC-MS analysis, will frequently resolve the problem. Reducing the size of the sample aliquot injected into the GC (provided that detection limit requirements permit this) may also be helpful.

Poor Recoveries of Isotopically-labeled PCDD/PCDF Internal Standards Coupled with Detection of Little or No Native PCDD/PCDF in the Analysis.

Failure to detect the 13C-labeled PCDD/PCDF internal standards which were added to the sample prior to extraction in the final extract analyzed is often indicative of a shift in the elution profile of the alumina column used in sample cleanup. This is frequently attributable to excessive quantities of extraneous materials in the sample extract which is introduced onto the alumina column, and results in elution of the PCDD/PCDF in eluate fractions which are normally discarded rather than in the expected eluate fraction which is collected and subjected to further cleanup. In such cases, if the column eluate fractions which are normally discarded are retained until completion of the initial analysis, then these fractions can be further processed and analyzed later to determine whether or not these contain the "lost" PCDD/PCDF. Alternatively, either the alumina column or the carbon column used in cleanup may have retained the PCDD/PCDF entirely. In these instances, modification of the eluting solvent mixtures, that is, use of a "stronger" solvent in eluting the liquid chromatography column will sometimes yield recovery of the missing PCDD/PCDF. However, this may also increase the quantities of extraneous compounds in the final extract subjected to GC-MS analysis.

Failure of the Gas Chromatographic Column to Yield Required Resolution of Particular PCDD/PCDF Isomer.

When the overall quality of the observed mass chromatogram is reasonably good (that is, the presence of large quantities of extraneous materials on the sample extract is not indicated), but the resolution standard check mixtures indicate that specific PCDD/PCDF isomers which are

required to be separated uniquely are not resolved by the GC column, then the column may have degraded and replacement may be necessary. Such observations may also be indicative of a "dirty" GC sample injector and/or of the accumulation of large deposits of sample residues at the front end of the capillary GC column. In these cases, cleaning the sample injector and/or removing the first few inches of the capillary GC column will often correct the problem.

Inadequacy of Low-Resolution MS for Resolving Interferences to PCDD/PCDF Mass Chromatographic Peaks

In cases where low-resolution MS has been used in the GC-MS analysis, and interferences to PCDD/PCDF peaks are observed in the mass chromatogram, but these are not attributable to the factors just described and are not eliminated by the corrective actions recommended, then the use of high-resolution MS may be indicated. Whether or not this will be effective can usually be determined only by comparing the low-resolution MS and high-resolution MS results.

Typical Data Obtained in the Analyses of Ambient Air Samples for PCDD/PCDF

Some typical data obtained in the analyses of ambient air samples (combined filter/particulates and PUF cartridge) collected in the vicinity of a municipal refuse incinerator, using the analytical methods described herein, are shown in tabular form in Tables 5, 6, and 7. These data fully satisfy the criteria specified for identification of PCDD/PCDF in an earlier section. Table 5 shows the measured concentrations of the total tetra-, penta-, hexa-, hepta-, and octachlorinated CDD and CDF which were found in twelve ambient air samples and in a laboratory blank. The recoveries of the internal and surrogate standards added to these samples prior to processing, which were achieved in these analyses, are given in Table 6. As can be seen, these recoveries are excellent, indicating the efficacy of the analytical methodology. Finally, Table 7 shows the corresponding concentrations of the 2,3,7,8-substituted PCDD/PCDF which were measured in the ambient air samples analyzed here.

Mass chromatograms for one of the samples for which data are presented in Tables 5-7, sample number AST1-5, are shown in Figures 1-6. These are illustrative of the mass chromatograms obtained for all of the ambient air samples in the group analyzed here. These chromatograms generally illustrate excellent peak shapes, and are quite "clean," showing few interferences.

Table 5: Wright State University, Dayton, Ohio 45435
Analyses for Total Chlorinated Congener Groups of PCDD and PCDF
Column - DB-5, 60M, 0.25 μ

	Concentrations Found (femtograms per M^3)									
Ambient Air Sample #	Tetra CDFs	Tetra CDDs	Penta CDFs	Penta CDDs	Hexa CDFs	Hexa CDDs	Hepta CDFs	Hepta CDDs	Octa CDF	Octa CDD
AST1-1	280	12	38	ND 19	67	100	ND 25	340	59	900
AST1-2	1100	390	1100	2900	360	1400	390	1000	100	1200
AST1-3	290	30	170	ND 23	140	210	190	630	100	1500
AST1-10	300	43	210	220	250	150	130	390	97	800
AST1-11	230	53.2	230	180	310	120	220	490	130	1000
AST1-QA (Lab Blank)	ND 3.1	ND 3.9	ND 3.2	ND 10	ND 5.2	ND 5.3	ND 7.6	50.7	ND 13	270
AST1-4	680	92	860	590	780	390	400	670	130	1200
AST1-5	1600	140	1900	1300	1600	640	660	1100	200	1700
AST1-6	1200	100	1200	680	830	420	400	620	120	1100
AST1-8	130	17	170	240	190	300	97	740	53	1300
AST1-9	230	36	380	320	410	290	190	500	61	770
AST9-25	480	ND 43.7	460	350	360	120	410	810	ND 182	9500
AST9-27	260	38	330	290	210	270	210	240	83	970

a. The designation ND indicates "None Detected" in excess of the minimum detectable concentration which is listed directly below the ND designation.

Table 6: Recoveries of Internal and Surrogate Standards
Wright State University, Dayton, Ohio 45435
Column - DB-5, 60M, 0.25 μ

Percent Recoveries of Internal and Surrogate Standards										
Ambient Air Sample #	%Rec. 1	%Rec. 4	%Rec. 7	%Rec. 9	%Rec. 11	%Rec. 14	%Rec. 17	%Rec. 19	%Rec. 20	Ave. % Rec.
AST1-1	67	93	99	102	91	92	85	99	83	90
AST1-2 RC	85	80	77	87	87	88	82	84	68	82
AST1-3	85	98	106	115	89	99	95	119	105	101
AST1-10	80	126	131	161	126	149	144	180	148	138
AST1-11	74	90	94	95	84	97	85	97	83	89
AST1-QA	76	94	98	110	75	95	87	105	90	92
AST1-4	91	79	85	92	92	104	96	102	101	94
AST1-5	100	85	90	103	98	114	108	114	112	103
AST1-6	94	83	86	96	91	107	99	107	112	97
AST1-8	87	77	79	89	83	101	92	102	89	89
AST1-9	92	78	82	92	92	107	96	104	109	95
AST9-25	83	73	70	79	70	80	66	59	49	70
AST9-27	81	75	79	88	79	93	79	72	65	79
Int. Std. Ave. Rec.	84	87	90	101	89	102	93	103	93	94
Std. Dev.	9	14	15	20	13	16	18	27	24	

1. The numbered standards are as follows:

1 = C_{13}-2378 TCDF
4 = C_{13}-1234 TCDF
7 = C_{13}-12378 PeCDF
9 = C_{13}-12378 PeCDD
11 = C_{13}-123678 HxCDF
14 = C_{13}-123478 HxCDD
17 = C_{13}-1234678 HpCDF
19 = C_{13}-1234678 HpCDD
20 = C_{13}-OCDD

Table 7: Wright State University, Dayton, Ohio 45435
Analyses for 2378-Substituted Dioxins and Furans
Columns - DB-5 and DB-Dioxin, 60M, 0.25 μ

Concentrations Found (femtograms per M^3)[a]

Ambient Sample #	AST1-1	AST1-2	AST1-3	AST1-10	AST1-11	AST1-QA (blank)	AST1-4	AST1-5	AST1-6	AST1-8	AST1-9	AST9-25	AST9-27
2378 TCDF	40.1	220	55.4	46.6	43.8	ND(3)	129	253	169	39.5	42.9	ND(26)	42.0
2378 TCDD	ND(9)	ND(4)	ND(7)	ND(3)	ND(3)	ND(4)	ND(5)	ND(8)	ND(5)	ND(5)	ND(3)	ND(44)	3.03
12378 PeCDF	ND(13)	48.0	ND(8)	17.2	17.8	ND(4)	56.3	116	61.3	ND(9)	21.9	ND(130)	ND(20)
23478 PeCDF	ND(17)	74.7	ND(18)	18.1	ND(5)	ND(3)	76.9	174	80.3	ND(14)	38.1	ND(120)	27.3
12378 PeCDD	ND(19)	97.4	ND(23)	ND(27)	ND(33)	ND(10)	50.7	137	51.5	35.6	ND(39)	ND(110)	33.5
123478 PeCDF[b]	ND(23)	ND(8)	39.4	48.1	63.8	ND(4)	72.8	137	66.3	17.8	38.1	ND(40)	36.9
123678 HxCDF	23.7	90.1	ND(33)	39.2	52.7	ND(7)	138	356	140	ND(33)	65.3	356	61.0
234678 HxCDF	25.3	76.0	ND(18)	29.5	24.6	ND(5)	73.4	153	76.4	35.8	41.6	ND(100)	34.3
123789 HxCDF	ND(4)	ND(11)	ND(11)	ND(3)	ND(4)	ND(6)	ND(4)	10.6	4.58	ND(4)	ND(2)	ND(54)	3.49
123478 HxCDD	ND(19)	41.3	30.1	9.31	17.4	ND(6)	21.3	49.5	23.0	23.2	21.0	ND(80)	13.8
123678 HxCDD	ND(19)	87.6	23.5	30.8	23.7	ND(6)	44.0	76.7	36.2	35.8	37.1	ND(83)	ND(23)
123789 HxCDD	ND(24)	41.9	ND(29)	16.5	23.2	ND(5)	ND(25)	68.1	52.1	30.3	44.7	ND(66)	33.3
1234678 HpCDF	ND(46)	235	92.6	109	111	ND(8)	350	467	271	76.5	137	411	123
1234789 HpCDF	ND(34)	37.8	ND(22)	20.5	23.3	ND(10)	34.5	ND(53)	32.4	ND(13)	19.2	ND(73)	18.2
1234678 HpCDD	177	447	327	198	233	31.5	316	525	292	350	348	805	239
OCDF	59.3	ND(10)	101	97.3	110	ND(13)	131	199	119	ND(6)	60.8	ND(180)	82.7
OCDD	902	ND(15)	1548	803	1036	269	1170	1665	1082	1317	769	9465	969

a. "ND" indicates "None Detected" in excess of the minimum detectable concentration which is listed directly below the "ND" designation.

b. This isomer may be convoluted with other isomers of its congener group.

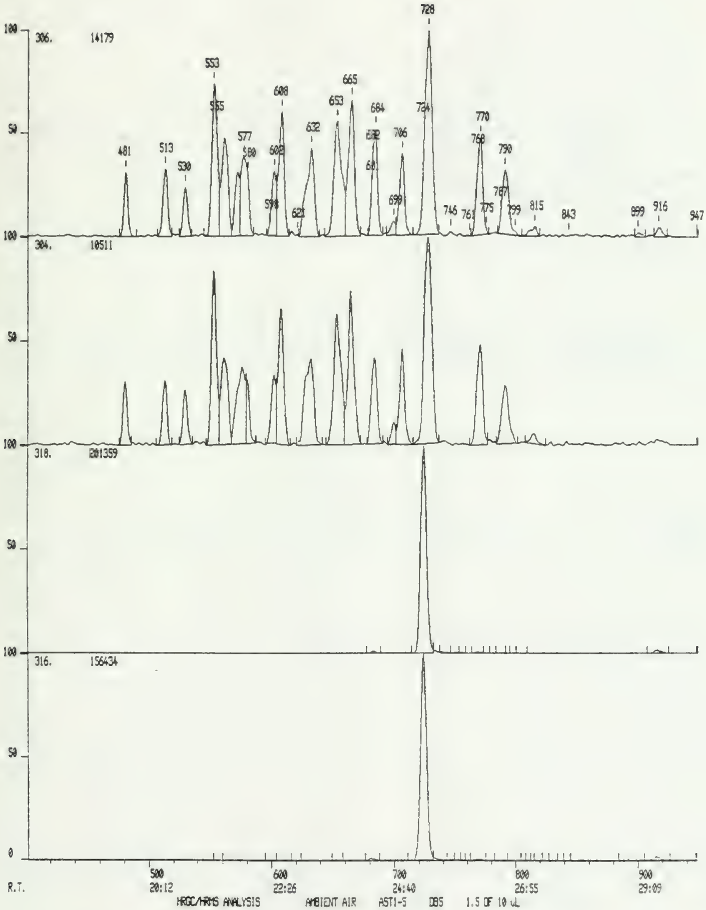

Figure 1: Selected-Ion Mass Chromatograms for Tetrachlorodibenzofurans

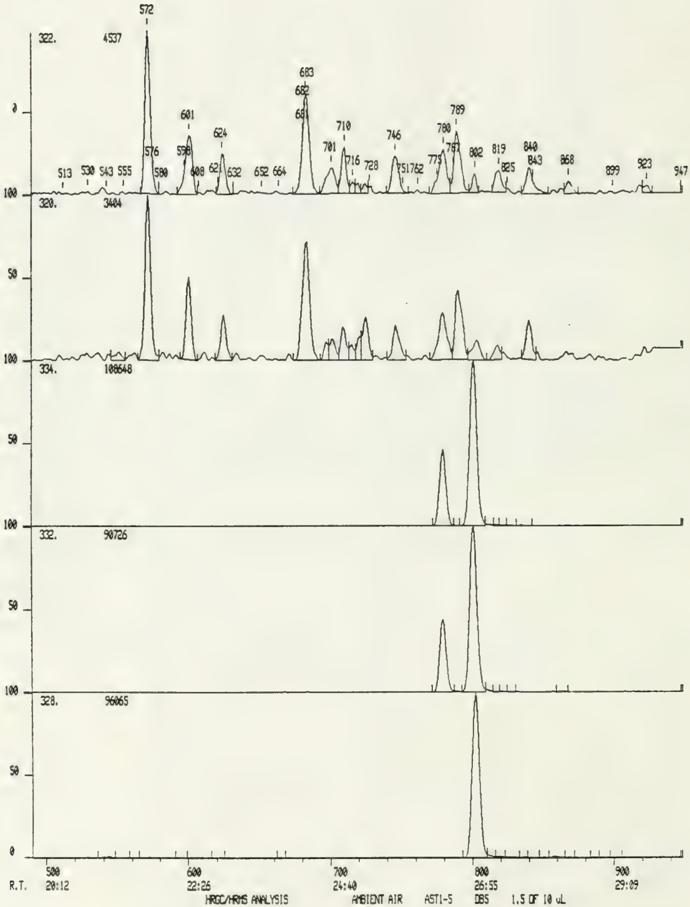

Figure 2: Selected-Ion Mass Chromatograms for Tetrachlorodibenzo-p-dioxins

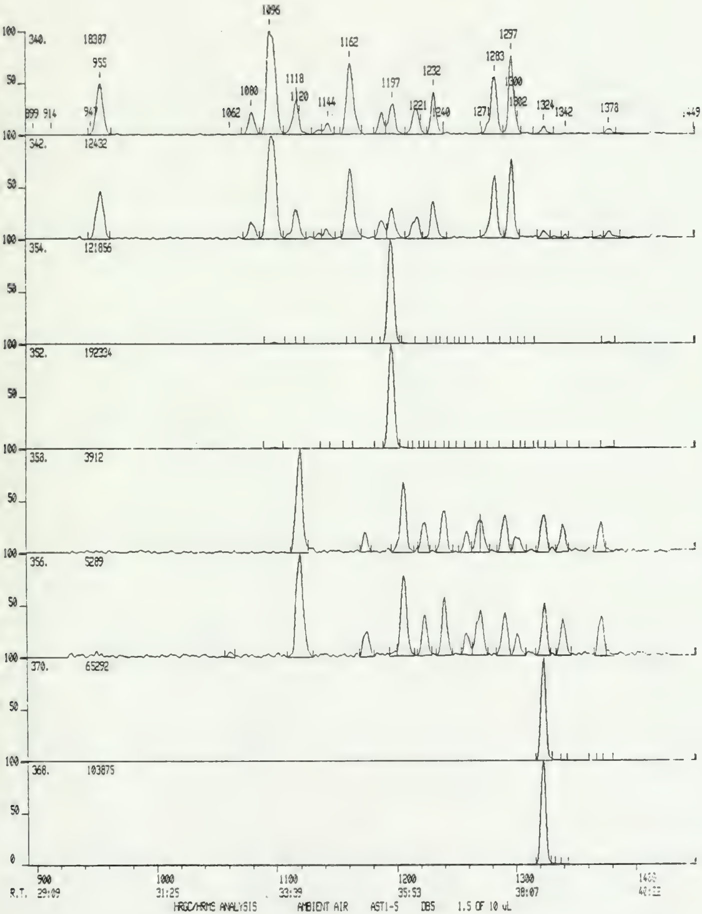

Figure 3: Selected-Ion Mass Chromatograms for Pentachloro- Furans & Dioxins

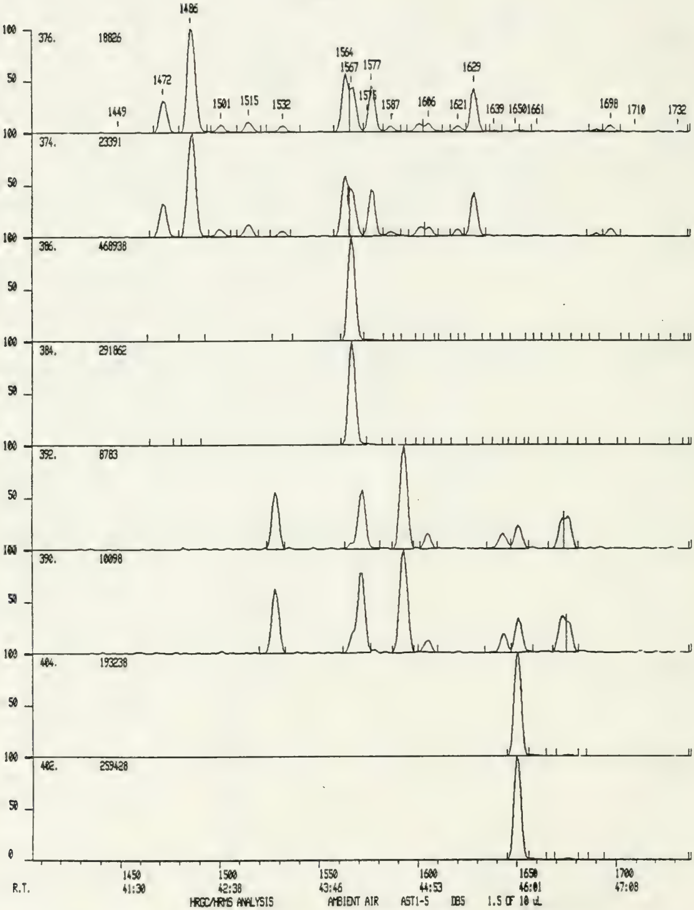

Figure 4: Selected-Ion Mass Chromatograms for Hexachloro- Furans & Dioxins

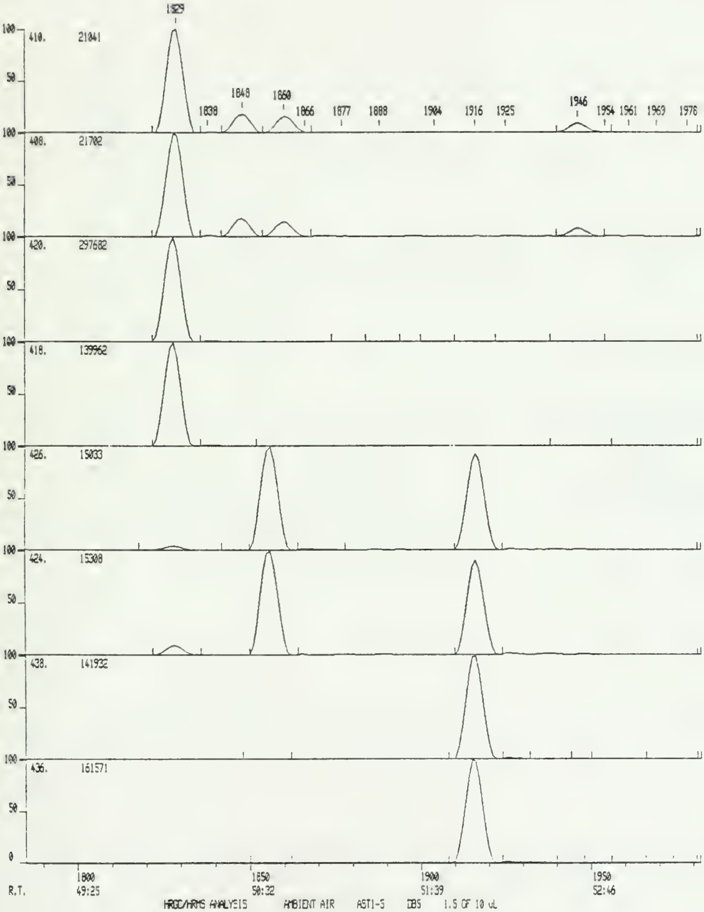

Figure 5: Selected-Ion Mass Chromatograms for Heptachloro- Furans & Dioxins

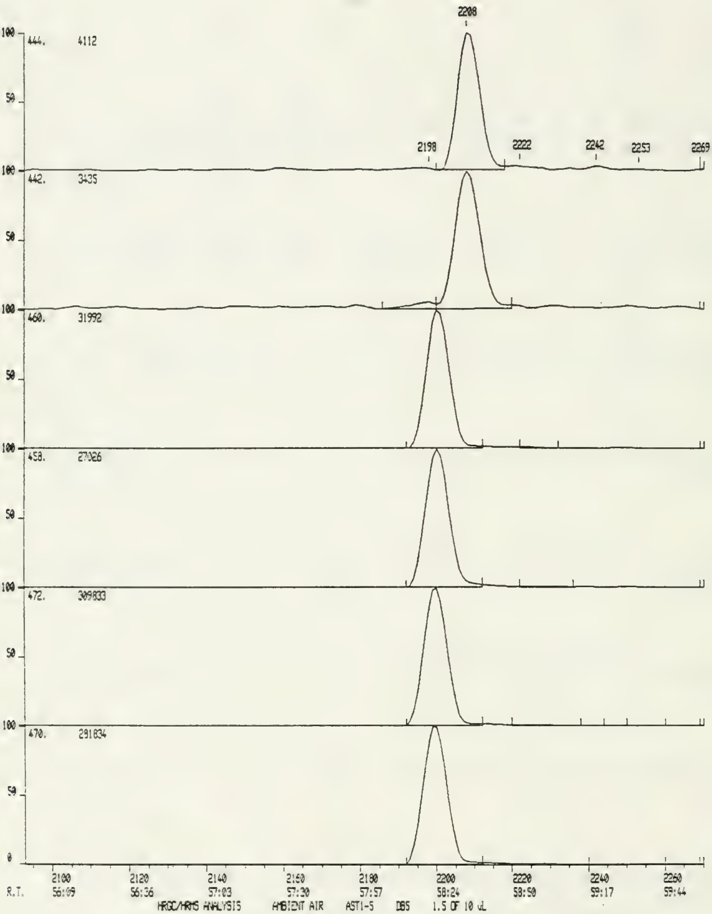

Figure 6: Selected-Ion Mass Chromatograms for Octachloro- Furans & Dioxins

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Chapter 4

High Resolution Mass Spectrometric Method for the Analysis of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air Samples

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SUMMARY

A High Resolution Mass Spectrometric (HRMS) method has been developed for measuring ultra-trace amounts (fg/M^3) of PCDDs/PCDFs in ambient air samples. Results for a selected sample, analyzed by using both high resolution and low resolution mass spectrometric (LRMS) methodologies, are compared and discussed.

INTRODUCTION

Levels of PCDD/PCDF in the ambient air of several selected Canadian cities have been monitored by Environment Canada since 1987. One of the main objectives of this monitoring effort is to assess the environmental impact associated with the operation of municipal solid waste incinerators in the vicinity of urban areas. Hi-volume ambient air samples collected in these areas had been routinely analyzed by Chemistry Division at RRETC using a Low Resolution Mass Spectrometric (LRMS) method until late 1989. Since that time, a High Resolution Mass Spectrometric (HRMS) method has been developed and applied to the analysis of these ambient air samples.

This chapter describes the latest analytical methodology employed by the Chemistry Division for the determination of PCDD/PCDF in ambient air. Various aspects of the procedures, including personnel safety, waste disposal, sample preparation, GC/MS analysis and quality assurance are briefly outlined in the following sections. Detailed descriptions can be found in References 1-3.

PERSONNEL SAFETY

Because of the highly toxic properties of PCDD/PCDFs, special precautions must be taken to minimize the risk of human exposure, either through direct contact with contaminated materials, or through inhalation of contaminated air. All work related to PCDD/PCDF analysis, including the preparation, handling, and storage of all samples and standards, should be conducted within a specially designed laboratory. This facility would include the following design features:

- restricted access area;
- sufficient ventilation;
- negative pressure relative to surrounding areas;
- all exhaust air ducting routed to a common, scrubbed outlet;
- segregation, via doors and air pressure differentials, into low and high hazard areas;
- an independent back-up air supply system designed to come into operation whenever a shut-down of the building's air supply system occurs;
- capability on auxiliary power in the event of a commercial power failure;
- capability to visually monitor ventilation system performance;
- devices to monitor indoor air levels of organic vapours generated from solvents used;
- a system of distinctive audio and visual alarms to alert lab personnel to potentially hazardous conditions.

Lab workers must wear protective clothing consisting of safety glasses, disposable coveralls, disposable foot coverings (optional) and disposable gloves. Other personal protective devices, such as face masks and cartridge or canister respirators, should be available in the laboratory in the event of a spill or other accident with potential to generate toxic fumes. Common laboratory safety equipment and facilities, such as safety showers, first-aid kits, eye wash stations and fire extinguishers, must be easily accessible.

WASTE DISPOSAL

Solid waste produced in the sample preparation laboratory includes disposable lab clothing, pipet tips, paper wipers, filter papers, spent chemicals from sample processing, sample residues and sample vials. These wastes are first sealed in polypropylene bags and then stored and sealed in large aluminum or durable plastic containers. These solid waste containers are temporarily stored in a locked, restricted access area and ultimately disposed of according to provincial disposal requirements for this class of wastes.

All solvent waste from sample processing and glassware cleaning operations is collected in 23-litre steel cans. A sample of waste solvents from each filled waste can are routinely analyzed for PCB and PCDD/PCDF. If the levels of these compounds are within the limits of provincial regulations, the waste is disposed through a licensed private contract company. Otherwise, contaminated wastes are stored on site until a suitable method for disposal is developed by the responsible federal and provincial authorities.

SAMPLE PREPARATION

Field samples consisting of polyurethane foam (PUF) and glass fiber filters are prepared for ultimate mass spectrometric analysis through a series of comprehensive extraction and cleanup steps. These procedures are schematically summarized in Figure 1 and are briefly described in the following sections.

Extraction

The sample (PUF and filter) is first spiked with 100 uL of surrogate solution containing 9, carbon-13-labelled, PCDD/PCDF congeners (2,3,7,8-substituted), at concentrations of 10-20 pg/uL (see Table 1). After 30 minutes of air drying, the sample is loaded into a soxhlet apparatus and extracted for 20 hours with toluene. The extract is then concentrated to 2 mL by rotary evaporation at 72°C or lower. After adding 100 mL of hexane, the extract is concentrated again to 2 mL at 30°C. The concentrated extract is passed through sodium sulphate with 50 mL of hexane rinse to remove any moisture retained in solvents. The extract is concentrated once more to 2 mL and is ready for sample cleanup.

Cleanup

Cleanup columns required in this method are illustrated in Figure 2.
The first Acid/Base column contains layers of sodium sulphate, silica, 44% (w/w) sulphuric acid on silica, 33% (w/w) of 1 M sodium hydroxide on silica and 10% (w/w) silver nitrate on silica. By chemical reaction, this column removes easily oxidized organics and sulphurous compounds from the raw extract. The prepared Acid/Base column is first washed with 30 mL of 2% dichloromethane (DCM) in hexane. The concentrated raw extract is then transferred onto the column, followed by adding 60 mL of 2% DCM in hexane. Column eluent is collected and concentrated to 2 mL by rotary evaporation. Finally, it is exchanged to hexane by adding 100 mL of hexane and repeating the concentration step.
The second column is a basic alumina column which can isolate PCDD/PCDF from most potential interferents by using adsorbent column chromatography. After pre-washing the activated basic alumina column with 15 mL of hexane, the concentrated extract from the Acid/Base column is transferred onto the basic alumina column, followed by three 5 mL hexane rinsings of the sample flask. An additional 30 mL of hexane is added to the column. Then, just as the solvent drains to the top of the sodium sulphate layer, 20 mL of 1.5% DCM in hexane is added.
The basic alumina column eluent, collected to this point, is labelled as fraction 1 and archived. When the solvent level in the column again just reaches the top of the sodium sulphate layer, 30 mL of 50% DCM in hexane is added and allowed to drain completely to a new flask. This fraction of eluent (fraction 2), containing the PCDD/PCDF, is concentrated to 2 mL and exchanged to hexane by adding 100 mL of hexane to the sample flask and repeating the concentration step. Cleanup procedures are repeated once more on a second alumina column. Fractions 1 from both alumina columns are combined and may be assessed for PCDD/PCDF if poor surrogate recovery is observed. Fraction 2, containing the PCDD/PCDF is transferred to a

Filter and PUF

Spike with Surrogates

20 hr. Soxhlet Extraction with Toluene

Concentrate (2 mL)

Exchange Solvent to Hexane

Dry over Na_2SO_4

Acid/Base Column

Exchange Solvent to Hexane

Basic Alumina Column

Repeat Basic Alumina Column

Concentrate PCDD/PCDF Fraction to Just Dryness

Add 20 μL of Recovery Standard Solution

HRGC/HRMS Analysis

Figure 1: Extraction, Cleanup, and Analysis Schematic

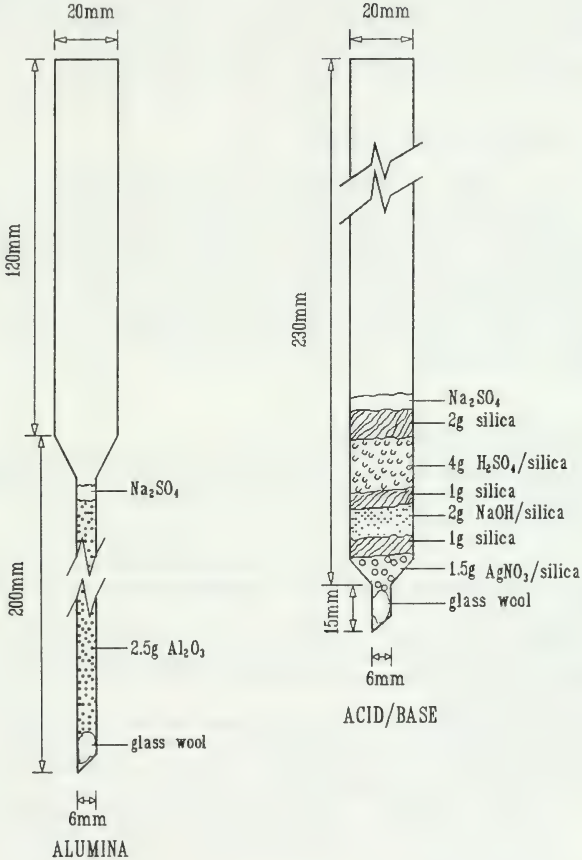

Figure 2: Cleanup Columns

1 mL conical vial and concentrated to a small volume under a gentle stream of pre-purified nitrogen. Prior to GC/MS analysis, the sample is blown down just to dryness. An exact volume of 20 uL of the recovery standard solution, containing 50 pg/uL each of $^{13}C_{12}$-1,2,3,4-TCDD and -1,2,3,7,8,9-H_6CDD in toluene, is added to the sample vial. The capped sample vial is then sonicated in an ultrasonic bath for one minute before GC/MS analysis.

INSTRUMENTAL ANALYSIS

Instrumental analysis of the prepared sample extracts is carried out using a high resolution gas chromatograph (HRGC) coupled to a high resolution mass spectrometer (HRMS). The gas chromatograph is equipped with a capillary column and is directly coupled to the mass spectrometer. The mass spectrometer is a double focusing unit supported by a dedicated computerized data system (DS). Sample analysis and data collection is carried out with the spectrometer operating in electron impact (EI) mode under the selected ion monitoring (SIM) technique. This sophisticated analytical device (HRGC/HRMS/DS) is capable of measuring extremely small quantities (femtogram amounts) of the target PCDD/PCDF analytes in the cleaned sample extracts.

Gas Chromatographic Parameters

A commercially-available Window Defining Mixture (WDM), which contains the earliest and latest eluting congeners in each PCDD/PCDF homologous group, is used to establish optimal gas chromatographic parameters and precise retention time windows for the time-sequenced SIM mode analysis of PCDD/PCDFs.

The order of elution on a 60 meter DB-5 column is such that five retention time windows can be defined, corresponding to the five levels of chlorine substitution (4 Cl to 8 Cl) without any overlap.
This mixture should be analyzed at regular intervals for verification of retention time windows. The WDM must be analyzed following any deliberate change in GC parameters; following any condition or upset which requires disconnecting the GC column; and following replacement of the carrier gas cylinder.
To achieve acceptable gas chromatographic separation one can use the following set of experimental parameters as a starting point:

- Injector temperature: 300°C for split-splitless or ambient for on-column;
- Interface temperature: 290°C;
- Temperature program: 1) Initial temperature at 100°C for split-splitless or 70°C for on-column and hold for 1 minute; 2) 100°C (or 70°C) to 200°C @ 40°C min^{-1}; 3) 200°C to 235°C @ 3°C min^{-1} and hold for 10 min; (4) 235°C to 310°C @ 8°C min^{-1} and hold for 15 min.

Isomer-Specific Separation

Using helium as carrier gas with an appropriate column velocity and oven temperature program as defined above, a 60-meter DB-5 column (0.25 mm ID, 0.25 um film thickness) can adequately separate 2,3,7,8-TCDD from neighbouring isomers 1,2,3,7-/1,2,3,8- and 1,2,3,9-TCDD. In addition, this column easily separates to baseline both hepta-CDD isomers (1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-) and the four hepta-CDF isomers (1,2,3,4,6,7,8-, 1,2,3,4,6,7,9-, 1,2,3,4,6,8,9- and 1,2,3,4,7,8,9-). However, on a DB-5 column 2,3,7,8-TCDF cannot be resolved from its neighboring isomers (1,2,4,9-, 2,3,4,8- and 2,3,4,6-). In order to quantify 2,3,7,8-TCDF accurately, use of an additional column (DB-225) is required. On a 30 m DB-225 column 2,3,7,8-TCDF can be resolved from its neighbouring 2,3,4,7- and 1,2,3,9-isomers.

For 2,3,7,8-TCDD and 2,3,7,8-TCDF analysis, a column performance test mixture, containing the target analyte and its neighboring isomers at equal concentration, should be analyzed daily to confirm acceptable chromatographic separation. It is recommended that these isomers be included in the Window Defining Mixture. The peak/valley criterion between 2,3,7,8-TCDD and its neighboring isomers should be equal to or less than 25% of the 2,3,7,8-TCDD peak height. The corresponding peak/valley criterion for 2,3,7,8-TCDF is 30% or less. Results for these analytes must be flagged if these criteria cannot be met in order to acknowledge the possibility of co-eluting isomers. Figure 3 illustrates acceptable chromatographic resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Mass Spectrometric Parameters

The mass spectrometer is operated in the electron impact mode with the ionization energy kept constant at a value ranging between 28 and 40 eV. The mass spectrometer must be tuned, using PKF, to achieve a resolution of at least 10,000 (10% valley definition). A lock-mass is assigned and monitored for each homologue window and its intensity must not vary by more than 10% throughout its respective window.

Sample components are identified as PCDD/PCDFs if their GC/MS data satisfy the following criteria:

(a) Peak responses for each of the two selected molecular cluster ions must be at least three times the background noise level;

(b) Chlorine isotope ratio for the two molecular cluster ions must be within $\pm$ 15% of the correct ratio;

(c) Peak maxima for both quantitation ions must coincide within two seconds;

(d) Response of the chlorinated diphenyl ether ion must be absent or insignificant relative to analyte peaks for PCDF determination;

(e) The relative retention time for 2,3,7,8-substituted congeners must agree with the calibration standards within 0.2%.

Calibration

Calibration standards should contain:

(a) all seventeen 2,3,7,8-substituted PCDD/PCDF congeners;

(b) the set of carbon-13-labelled congeners added to samples as surrogates;

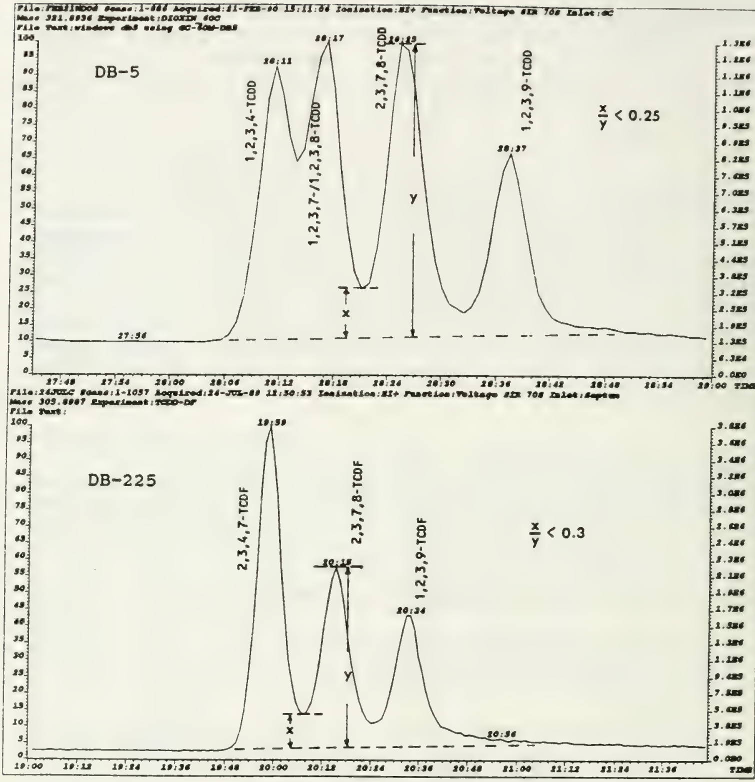

Figure 3: Acceptable Chromatographic Separation for 2,3,7,8-TCDD and 2,3,7,8-TCDF

(c) the labelled congeners $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HCDD which are added to sample extracts as (i) recovery standards to calculate surrogate recoveries; and (ii) reference peaks for assigning sample peak identities on the basis of relative retention times.

The linear calibration range for each analyte should be established by running a series of five multi-point calibration standards, in triplicate, prior to initial sample analysis. The recommended concentration levels for HRMS calibration standard solutions are presented in Table 1.

An Internal Standard method is recommended for quantitation of sample data. This method relies upon consistent linearity of MS response over the intervals between multi-point calibration checks and is easily integrated into automated routines for data quantitation (see Reference 3 for detailed procedures).

Internal Standard quantitation is based on the use of Relative Response Factors (RRF). A RRF is the ratio of analyte response factor (area counts per unit mass) to the response factor of the corresponding labelled surrogate. These RRFs remain unchanged over the range of concentration for which MS response is linear. Using these RRFs, along with surrogate responses from the sample run, concentrations of PCDD/PCDFs can be calculated directly, without the necessity of calculating surrogate recoveries. Recoveries should nevertheless be calculated separately and reported, as these values serve to indicate the overall quality of the concentration data being reported.

Limit of Detection

The Method Detection Limit (MDL) for PCDD/PCDF analysis is defined as the minimum concentration of analyte in the sample extract that will produce a clearly defined peak with an acceptable chlorine isotope ratio, and with a signal-to-noise ratio equal to 3-to-1. Variables such as sample matrix, sample size, final extract volume, injection volume used in analysis, surrogate recovery, GC column performance, chromatographic parameters, electronic noise and instrument sensitivity can directly influence the MDL.

Reported MDL must be corrected for surrogate recovery and is calculated as follows:

$$MDL = \frac{3 \cdot N \cdot A/H \cdot Q_s}{A_s \cdot RRF_n \cdot V}$$

where:

N = estimated sum of electronic and chemical (matrix) noise expressed in peak height;

A/H = area/height ratio for the surrogate standard peak;

Q_s = mass of the surrogate standard added (pg);

A_s = surrogate peak area;

RRF_n = relative response factor (native standard to surrogate standard);

V = sample size (M^3);

Method Detection Limits should be determined on a homologue by homologue and sample by sample basis. In cases where a quantitation ion chromatogram contains at least one peak which is sufficiently large to prevent observation of noise, the ion chromatogram should be rescaled to allow for measurement of noise amplitude. An example of noise determination is provided in Figure 4.

QUALITY ASSURANCE

Key elements of an acceptable quality assurance program that must be followed are summarized below.

(a) Prior to the processing of actual test samples, all pre-cleaned glassware (including Soxhlet apparatus, concentrators, columns, flasks, and vials) are rinsed with dichloromethane and hexane. Rinses are combined and processed in the same manner as test samples. If any amount of analyte is detected in the proof rinse, all glassware is washed again with appropriate solvents and a second proof rinse sample is collected for analysis.

(b) A method blank sample, consisting of clean sampling media spiked with surrogates, is processed with each batch of 10 test samples to demonstrate freedom from PCDD/PCDF cross-contamination.

(c) Prior to Soxhlet extraction, each sample is spiked with a mixture of 9 isotopically-labelled surrogates to assess the degree of analyte loss during sample work-up.

(d) Periodically, a control sample, consisting of blank sample media spiked with a mixture of native and surrogate analytes, is processed and analyzed along with routine samples. The analyte recoveries achieved gives an indication of the accuracy of the analyses.

(e) A known concentration of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD are added to each sample extract immediately prior to GC/MS analysis. These two compounds serve as retention time references for labelled surrogates and as the basis for calculation of surrogate recoveries.

(f) A Window Defining Mixture, containing the first and last eluting isomer within each congener group of PCDD/PCDFs, is used regularly to define retention time windows for Selected Ion Monitoring of individual congeners.

(g) Prior to sample analysis, calibration curves are constructed to verify linearity of MS response for all congeners over the concentration range of 0.25 to 400 pg/uL for PCDD/PCDFs.

(h) The established calibrations are verified by analyzing the calibration verification standard (CS3) at least once during every 8 hour period in which sample analysis occurs. The calculated concentration of each analyte must be within $\pm$ 15% of the design value. Recalibration is required if this criterion is not met.

(i) As a check on accuracy, NBS Reference Material 1614 (2,3,7,8-TCDD in solution) is periodically analyzed as a sample. This aspect of the QA program should be enhanced by the use of other reference materials, as they become commercially available.

Table 1: Composition of PCDD/PCDF Calibration Solutions for HRMS

PCDD/PCDFs Standard	pg/ul				
	CS1[a]	CS2	CS3[b]	CS4	CS5
Native Standards					
2,3,7,8-TCDD	0.25	1	5	25	100
2,3,7,8-TCDF	0.25	1	5	25	100
1,2,3,7,8-P_5CDD	0.50	2	10	50	200
1,2,3,7,8-P_5CDF	0.50	2	10	50	200
2,3,4,7,8-P_5CDF	0.50	2	10	50	200
1,2,3,4,7,8-H_6CDD	0.50	2	10	50	200
1,2,3,6,7,8-H_6CDD	0.50	2	10	50	200
1,2,3,7,8,9-H_6CDD	0.50	2	10	50	200
1,2,3,4,7,8-H_6CDF	0.50	2	10	50	200
1,2,3,6,7,8-H_6CDF	0.50	2	10	50	200
2,3,4,6,7,8-H_6CDF	0.50	2	10	50	200
1,2,3,7,8,9-H_6CDF	0.50	2	10	50	200
1,2,3,4,6,7,8-H_7CDD	0.50	2	10	50	200
1,2,3,4,6,7,8-H_7CDF	0.50	2	10	50	200
1,2,3,4,7,8,9-H_7CDF	0.50	2	10	50	200
OCDD	1	4	20	100	400
OCDF	1	4	20	100	400
Surrogates					
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-P_5CDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-P_5CDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-H_6CDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,7,8-H_6CDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,4,6,7,8-H_7CDF	100	100	100	100	100
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD[c]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-H_6CDD[d]	50	50	50	50	50

[a] also used to assess detection limits; [b] used daily to verify calibration; [c] retention time reference and recovery standard for tetra- and penta-CDD/CDF; [d] retention time reference and recovery standard for hexa-, hepta- and octa-CDD/CDF.

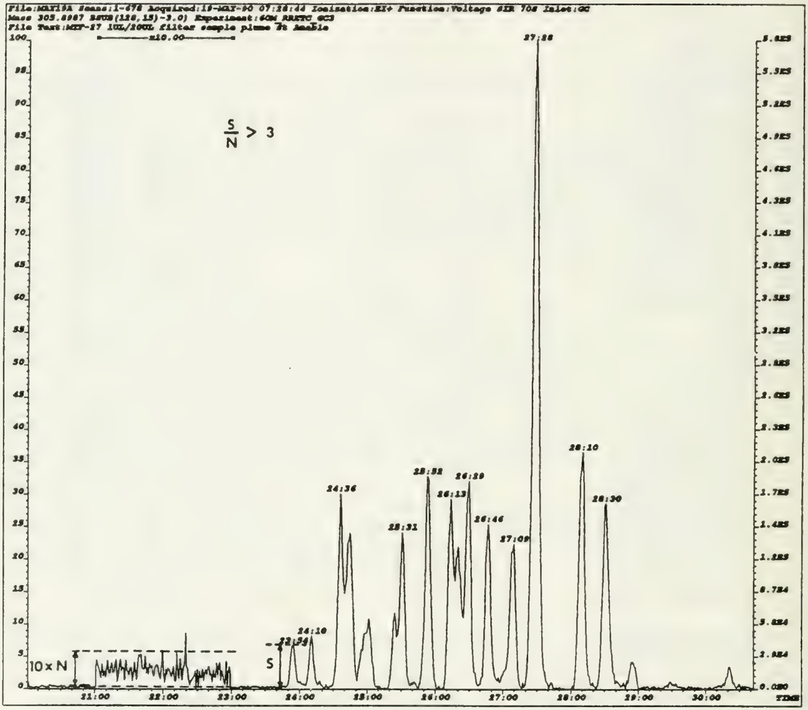

Figure 4: Noise Determination

(j) For 2,3,7,8-TCDD/TCDF analysis, acceptable chromatographic separation between these target analytes and their closest neighbouring isomers must be confirmed daily.

(k) Reported sample results are fully documented in terms of detection limits, surrogate recoveries, and number of isomer peaks contributing to reported homologue concentrations. All QA/QC documents and raw GC/MS data must be available for auditing.

RESULTS COMPARISON - LRMS VS HRMS

A selected ambient air sample containing significant amounts of PCDD/PCDFs was analyzed by both Finnigan 4500 quadrupole LRMS and VG70S double focusing HRMS at 10,000

TABLE 2 COMPARISON OF LOW RESOLUTION AND HIGH RESOLUTION MS RESULTS FOR A SELECTED AMBIENT AIR SAMPLE

ANALYTE	Finnigan 4500			VG 70S-10,00 Res.		
	pg/sample	NP	DL	pg/sample	NP	DL
TCDD	71	1	30	106	3	3
P_5CDD	ND	0	52	105	8	5
H_6CDD	510	2	58	429	3	6
H_7CDD	291	1	62	344	2	7
OCDD	384	1	86	381	1	12
Total PCDD	1256			1365		
TCDF	90	2	26	197	13	2
P_5CDF	ND	0	40	219	12	5
H_6CDF	105	2	46	180	7	5
H_7CDF	61	1	52	84	2	6
OCDF	32	1	80	25	1	9
Total PCDF	288			705		
2378-TCDD	ND	0	30	ND	0	3
2378-TCDF	76	1	26	58	1	1

Note: NP = number of analyte peaks; DL=detection limit in pg/sample

resolution. Comparative results with respect to concentrations, number of analyte peaks detected and detection limits (DL) are summarized in Table 2. Significant differences and agreements between the two sets of results are listed below.

- The HRMS data provided better (lower) sensitivity than the LRMS by a factor of 10.
- In general, the LRMS detected less analyte peaks than the HRMS. As a result, the total amount of PCDF detected by the HRMS is much greater than the result using the LRMS technique.
- While no P_5CDD and P_5CDF were detected by LRMS, a total of 8 and 12 analyte peaks, respectively, were found by the HRMS method.
- Both HRMS and LRMS results agree well on certain specific isomers (e.g. OCDD, OCDF and 2,3,7,8-TCDF) which were present at concentrations above the DL of the LRMS technique.

Discrepancy in reporting target analytes between these two methods is further illustrated using the TCDD and TCDF chromatograms in Figure 5. Checkmarks indicate peaks identified by HRMS as PCDD/PCDFs while shadow peaks represent target analytes identified by LRMS. Apparently, only one of three TCDD peaks and two of thirteen TCDF peaks were identified as positive analytes by LRMS because of the poorer sensitivity of this technique.
In addition to better sensitivity, the HRMS also provided superior selectivity. This is demonstrated by the fact that a major H_7CDD toxic congener (1,2,3,4,6,7,8-H_7CDD) was clearly identified by HRMS as the target analyte. The same congener peak detected by LRMS, however, failed to meet the isotope criterion because of interference problems.
In conclusion, data generated by HRMS is superior to that obtained by LRMS in terms of both sensitivity and selectivity. When using the LRMS procedure, matrix interferences often cannot be eliminated despite rigorous and repeated cleanup. In addition, the poorer instrument sensitivity mitigates against the production of useful data for ambient air dioxin monitoring. The complex nature of such samples and the low levels of PCDD/PCDFs in ambient air makes the HRMS procedure the method of choice.

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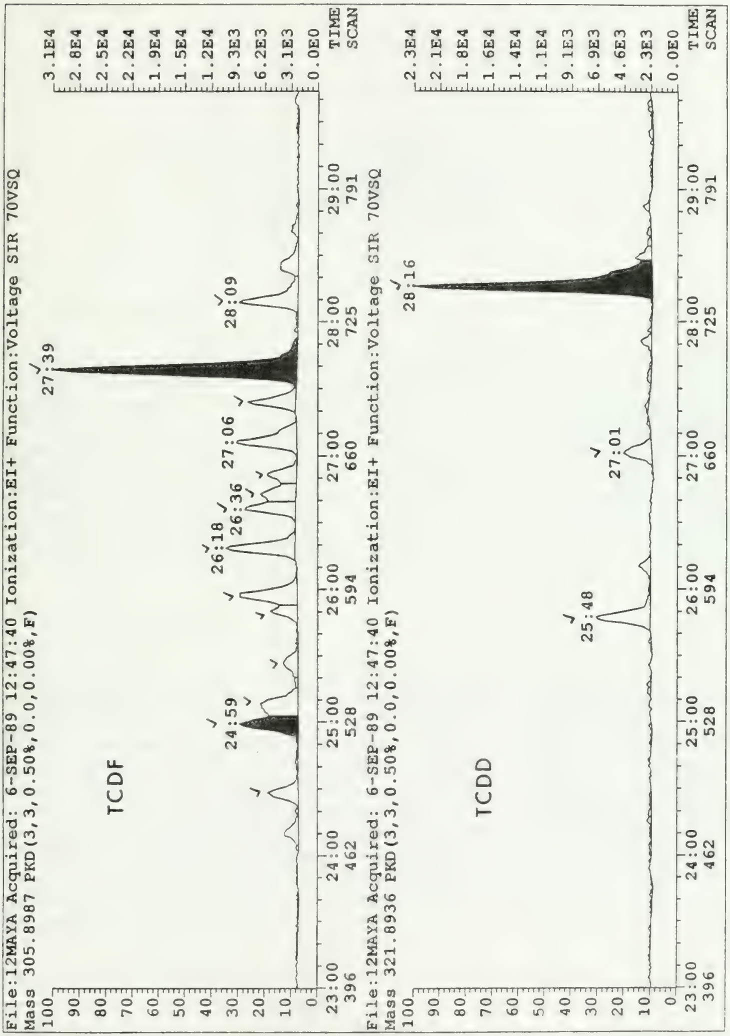

Figure 5: Example of Measurable TCDD and TCDF Congener Peaks

Chapter 5

Exposure Assessment - Data Requirements

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SUMMARY

Aspects of the exposure assessment part of risk assessment with emphasis on the multi-media exposure assessment aspects (that is combined exposures from air, soil, water, food, etc.) are discussed. The impact of data quality/availability on exposure estimates is highlighted by use of the Ministry of the Environment's (MOE) involvement with the multi-media exposure assessment for PCDDs/PCDFs (MOE, 1985, Birmingham et al, 1986, Birmingham et al, 1989b). The availability of better and more relevant monitoring data since 1985 has considerably refined our exposure estimate for PCDD and PCDF, however, more Canadian long-term monitoring data and good congener specific data are required to both sharpen our estimate of the toxicity of PCDD and PCDF mixtures and to better understand the sources of contamination of our food chain and other sources of human exposure.

INTRODUCTION

The Hazardous Contaminants Branch of the Ontario Ministry of the Environment is responsible for the interpretation of analytical data with respect to the following question: "What do these results mean in terms of human safety and/or environmental risk?". Aspects of the exposure assessment part of risk assessment with emphasis on the multi-media exposure assessment aspects and the impact of data quality/availability on exposure estimates will be discussed here. Through this process, areas where the exposure assessor requires more detailed analytical data will be highlighted. The Ministry of the Environment's (MOE) involvement with the multi-media exposure assessment for PCDDs/PCDFs (MOE, 1985, Birmingham et al, 1986, Birmingham et al, 1989b) will be used as an example to illustrate this process. The task has involved collaboration with many people at MOE, Health & Welfare Canada (HWC) and Environment Canada, whose contributions are gratefully acknowledged.

RISK ASSESSMENT OF PCDD/PCDF

This story actually starts in 1983 when Hazardous Contaminants Branch (HCB) embarked on producing a scientific criteria document on PCDD/PCDF. This document took the approach shown in Figure 1. The toxicological evaluation part (left hand side of Figure 1) was independent of the exposure assessment and involved the derivation of the tolerable daily intake (TDI) of 10 pg 2,3,7,8-T_4CDD toxicity equivalents (TEQ)/kg body wt (MOE, 1985, CEPA, 1990). The exposure assessment (right hand side of Figure 1) had to handle two difficult problems; one was the complexity problem related to the complex mixtures of PCDD and PCDF we are exposed to, and the other, was the ubiquity problem since PCDD/PCDF are persistent and found in all environmental media to a greater or lesser degree.

The first problem of complexity was addressed by the use of toxicity equivalency factors (TEF) which is discuss below. The second problem was addressed by using a multi-media exposure approach. This multi-media approach views the TDI as an umbrella intake value that the combined exposures from all media (that is exposures from air, soil, water, food, etc.) should not exceed. In the multimedia approach, we want to integrate all exposures when assessing the overall dose we are exposed to (Figure 2).

The use of TEF to tackle the complex mixture requires some discussion since several countries have developed these schemes and they are commonly used to describe the potential toxicity of PCDD and PCDF mixtures (Swiss Government, 1982; MOE, 1985; FRG, 1985; EPA, 1987; Nordisk Ministerrad, 1988). There is some loss of information on the actual levels and distribution of the various PCDD and PCDF congeners present which is valuable for identifying "source signatures" and for estimating source contributions. However, from a health assessment point of view, the calculated TEQ are useful for estimating the toxic potential of exposure to PCDD and PCDF mixtures and most animal tissues act as a biological filter to retain the 2,3,7,8-substituted congeners. Currently, the toxicological information suggests that we are looking at seventeen 2,3,7,8-substituted congeners as potentially the most toxic out of the total of 210 PCDD and PCDF congeners.

A recent development has been the proposal of an international TEF scheme so that a common approach can be taken to assessing the toxicity of PCDD and PCDF mixtures (NATO CCMS, 1988). The TEF scheme is based on the best toxicological data available and consequently is subject to future changes. As more information comes in on the chronic effects of these congeners these factors may be adjusted.

This TEF scheme is shown in Table 1 and has been adopted by Canada (CEPA, 1990), the U.S. (EPA, 1989) and some European countries, e.g., U.K., 1989. These factors (table 1) assume that congener-specific analyses of PCDD and PCDF mixtures are available. Toxicity

FIGURE 1. RISK ASSESSMENT

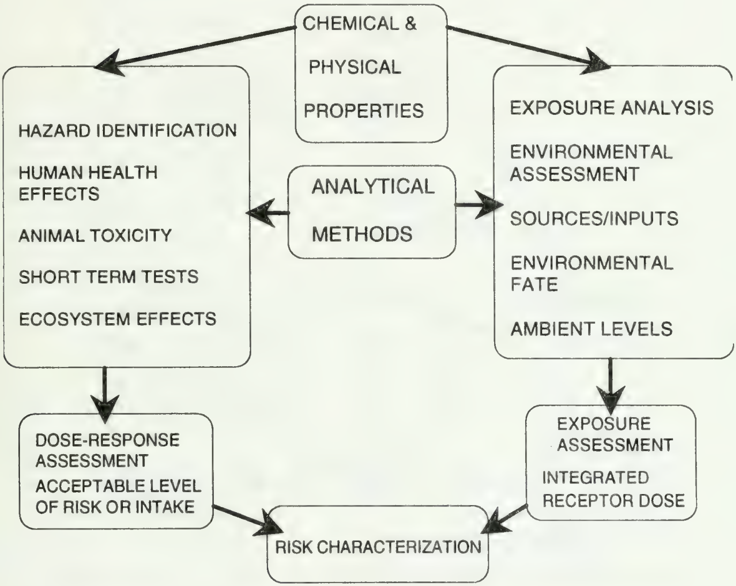

FIGURE 2. HUMAN EXPOSURE TO ENVIRONMENTAL CONTAMINANTS

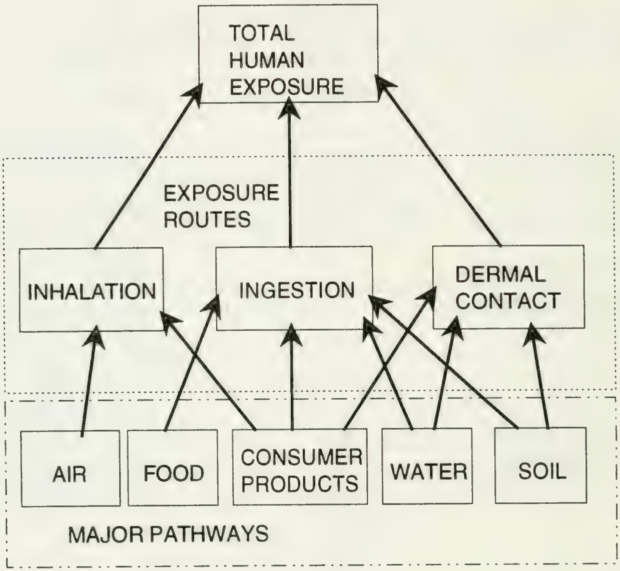

Table 1. International Toxicity Equivalency Factors (I-TEF) for Congeners of Concern

Congener of Concern	I-TEF
2,3,7,8-T_4CDD	1
1,2,3,7,8-P_5CDD	0.5
1,2,3,4,7,8-H_6CDD	0.1
1,2,3,7,8,9-H_6CDD	0.1
1,2,3,6,7,8-H_6CDD	0.1
1,2,3,4,6,7,8-H_7CDD	0.01
1,2,3,4,6,7,8,9-O_8CDD	0.001
2,3,7,8-T_4CDF	0.1
2,3,4,7,8-P_5CDF	0.5
1,2,3,7,8-P_5CDF	0.05
1,2,3,4,7,8-H_6CDF	0.1
1,2,3,7,8,9-H_6CDF	0.1
1,2,3,6,7,8-H_6CDF	0.1
2,3,4,6,7,8-H_6CDF	0.1
1,2,3,4,6,7,8-H_7CDF	0.01
1,2,3,4,7,8,9-H_7CDF	0.01
1,2,3,4,6,7,8,9-O_8CDF	0.001

equivalents (TEQ) are obtained by multiplying the analysed amounts of the particular congener by the appropriate factor. For a mixture the calculated TEQ are summed.

In the absence of analytical data that does not distinguish between 2,3,7,8- and non-2,3,7,8-substituted congeners, e.g., data reported as total isomeric group only, then several approaches can be used to estimate the relative quantity of 2,3,7,8- substituted congeners and so provide a more realistic estimate of the mixture's toxicity (Birmingham, 1990).

The first approach is the *worst case estimate* where all congeners are assumed to be 2,3,7,8-substituted (this approach may be prudent when no data on congener distribution are available). The second approach can be called the *proportional approach.* In this case existing congener-specific analyses are available from similar samples and may be used to estimate the proportion of 2,3,7,8- substituted congeners present. Another approach is called the *average case* approach, in this case congeners are assumed to be evenly distributed and the 2,3,7,8-substituted congeners contribution to the group is proportional to the number of isomers normally found in the group. This theoretical approach can be a good starting point but not all sources and formation processes for PCDD and PCDF allow for an even distribution of congeners in each isomer group.

The bottom line for analysts is that we need more congener- specific analyses. This requirement rings economic alarm bells because of increased costs and analysis time. However, we can approach this by using the congener-specific data of a representative subsample to provide enough information to calculate TEQ for the rest of the samples, i.e., the proportional approach.

EXPOSURE ASSESSMENT OF PCDD/PCDF

The primary purpose of an exposure assessment is to estimate the real world dose value for use in a dose-response relationship (Figure 1). Estimation of exposure can involve direct or indirect measurements. Direct measurements are made at the receptor/environment interface. Indirect measurements can be:

a) reconstructive; or
b) predictive.

Reconstructive measurements are based on levels found in the receptor or effects induced in the receptor and confirm exposure and may indicate the magnitude of the overall dose from all sources. Predictive measurements are based on measurements some distance from the receptor, e.g. source emissions/dispersion modelling/fixed location monitoring/ levels in various environmental media (air, food, soil, water, consumer products) and are not necessarily evidence of exposure but may suggest the potential amount that can reach the receptor.

Ontario has used a combination of modelling and monitoring data to estimate exposure from environmental media. Being a regulatory agency our mandate is to control or eliminate exposure to harmful substances. The regulatory equation is quite complex and includes factors for legal, technical control capability and socio-economic variables. On the scientific side, exposure assessment also requires knowledge of ambient background levels as well as modelled or measured emissions. A knowledge of the analytical capability to measure the chemical in the medium in question and the minimum detection limits is also required.

The accuracy of exposure estimates is very dependent on available data. As an example of how our understanding of PCDD and PCDF exposure has evolved, our 1985 exposure assessment based on MOE (1985) is shown in Table 2. In this case, the ambient air level was estimated from the results of dispersion modelling of incinerator emissions (using ground level concentration maximums on an annual average basis as an index of what a receptor near an incinerator might be inhaling), the water and soil data were based on Ontario monitoring data and the food data was based on limited data from Lake Ontario fish and episodes of known pentachlorophenol contamination of livestock. All these data were converted to TEQ and then calculated as the absorbed dose using various physiological models and assumptions. A casual glance at Table 2 would suggest that ambient air and fish are major sources of PCDD and PCDF exposure to an average urban adult. Improved analytical data have altered this assessment.

Since 1985, Ontario has collaborated with Health & Welfare Canada and Environment Canada to develop a national basis for developing multi-media environmental guidelines. This collaboration resulted in a detailed exposure assessment based on the most recent and reliable monitoring data available (Birmingham et al, 1989b). The air, water, soil and consumer products data is shown in Table 3. In this case, the ambient air data is based on long-term monitoring of the urban atmosphere at fixed locations in Niagara Falls, New York (New York State, 1985; Smith et al, 1985, 1986, 1987) and Bloomington, Indiana (Eitzer and Hites, 1986, 1987). At this time, we did not have the work of Buck and Kirschmer (1988) in Germany or the U.S. data of Gary Hunt (see this proceedings) or T. Tiernan (see this proceedings). The mean and range values take into account the seasonal variation in levels of PCDD and PCDF as well as monitoring locations ranging from downtown to suburban.

Analytical data needed to improve our exposure estimates include more Canadian long-term monitoring data and good congener-specific data. It would be interesting to compare urban and rural exposures, as well as the impact of indoor air on overall ambient exposure. By using congener-specific data from N.Y., Sweden and Germany, some proportional factors for calculating ambient air TEQ have been proposed (Birmingham, 1990). It can be seen that

Table 2: Summary of Exposure Assessment (Worst Case - 1985)

Environmental Compartment	Total PCDD and PCDF Concentration Range	2,3,7,8-T_4CDD Equivalents	Daily Dose[1] (Absorbed) (pg TEQ/kg/d)
Air (annual ambient ground level concentration)	28 pg/m^3	8.4 pg/m^3	2.1
Surface Water	0.002 ng/L	0.002 ng/L	0.05
Soil - Ingestion (children) - Dermal (children) - Dermal (adult)	4820 pg/g	81.1 pg/g	0.07 0.01-0.13 0.001-0.013
Food - Fish - Poultry - Pork - Eggs	20 ng/kg 400 ng/kg 500 ng/kg 100 ng/kg	20 pg/g 8.8 pg/g 0.8 pg/g 0.01 pg/g	4.7 0.7 0.3 0.007

1. 60 kg individual processing 20 m^3 air, 1.5L water, 1 g soil and Canadian average consumption factors (Health and Welfare Canada, 1977)

Table 3: Estimates of Concentrations of PCDD and PCDF in Substrates/Media (Based on ND Equal To Lowest Detection Limit)

Substrate or Media	Concentration in Medium		
	Data Set	Data Selected	Estimated Concentration in TEQ[1]
Air	Ambient air monitoring data for 22 Niagara Falls, N.Y. samples and 30 Bloomington, Indiana samples (NYDEC, 1985, Smith et al, 1986,1987; Eitzer and Hites, 1986, 1987)	Mean values 2.2 to 8.4 pg total PCDD + PCDF/m^3 range 0.4 to 36.7 pg total PCDD + PCDF/m^3	mean value 0.2 pg TEQ/m^3 range 0.03 to 0.91 pg TEQ/m^3
Water	Concentrations detected in Canadian drinking water (MOE, 1984, 1986, Jobb et al., 1990). Detection limit of 10 pg/L (over 800 samples)	ND - 46 pg O_8CDD/L	0.07 pg TEQ/L
Soil	Soils from urban backyards, public use areas and parkland 14 Ontario samples (McLaughlin et al, 1987) 13 Midwestern U.S. samples (U.S.EPA, 1985)	mean value 2700 pg total PCDD + PCDF/g range 50 - 14,100 pg total PCDD + PCDF/g	mean value 49 pg TEQ/g range 1 to 330 pg TEQ/g
Consumer Products	No Canadian data for drugs, cosmetics cigarettes or other consumer products	-	-
	- 9 bleached pulp and paper products (NCASI, 1987)	Range of ND (<1 ppt) to 14 ppt of 2,3,7,8-TCDD and to 250 ppt 2,3,7,8-TCDF	15 pg TEQ/g dry weight of paper products

1. Calculations based on average detected value. **Where data are reported as non-detected (ND) or absent then residues assumed present at the minimum reported detection limit.** TEQ are derived using international TEF values (NATO-CCMS, 1988; CEPA, 1990)

the estimated intake from inhalation of ambient air has dropped from 2.1 pg TEQ/kg/d (Table 1) to 0.07 pg TEQ/kg/d (Table 5).

Water (MOE, 1984, 1986) and soil (McLaughlin et al, 1989; U.S. EPA, 1985) values are based on a more extensive set of samples than that available in 1985. In the case of water, we need lower LOD since PCDD/PCDF are N.D. in most cases, however, residue levels in aquatic biota from some locations indicate the presence of PCDD and PCDF in water at some level.

Soil is currently an area of much interest since we are exposed to it as soil, dust, air particles or via vegetation uptake. More congener-specific data are needed here.

A category for exposure from consumer products has been included since data on PCDD and PCDF contamination of chlorine-bleached kraft pulp and paper products was not available in 1985 (NCASI, 1987). Of course, this whole area requires much more analytical data.

The food category (Table 4) has benefited greatly from the 1988 Ontario food basket study (MOE, 1988; Birmingham et al, 1989a). In this case, as well as more congener specific data on a wider range of foods, there is a need for more data on processed and packaged food as this can highlight sources of exposure between the field and the supermarket shelf. A good example of this is the discovery of PCDD/PCDF in milk cartons (Ryan et al, 1988; Rappe et al., 1989)

The highlights of this 1988 multi-media exposure assessment are shown in Table 5. From the perspective of the average urban adult, food (including fish) is the major exposure pathway with ambient air as a distant second. The availability of better and more relevant monitoring data since 1985 has considerably refined our exposure estimate for PCDD and PCDF, however, more congener specific data are required to both sharpen our estimate of the toxicity of PCDD and PCDF mixtures and to better understand the sources of contamination of our food chain and other sources of human exposure.

Table 4: Estimates of Concentrations of PCDD and PCDF in Food (Based on ND Equal to Lowest Detection Limit)

Concentration in Medium		
Data Set	Data Selected	Estimated Concentration in TEQ[1,2]
Fish - Smelt data as typical for commercial fish from Great Lakes (Ryan et al, 1984)	<2-12pg 2,3,7,8-TCDD/g <2-20pg total T_4CDD/g <2-8pg total P_5CDD/g	8.5 pg TEQ/g fresh wt (arbitary assignment of 5 pg/g smelt for each 2,3,7,8-T_4CDD, T_4CDF and P_5CDF)
Poultry - Limited Canadian data, 5 samples (Ryan 1987, MOE 1988)	All ND (1 to 6) except 15 pg H_7CDD/g fresh wt and 17, 26 & 210 pg O_8CDD/g - fresh wt	0.56 pg TEQ/g fresh wt (assume poultry meat contains 15% fat)
Beef - Limited Canadian data, 2 values for ground meat, 1 sample for organ meat & 5 values for steak (Ryan, 1987, MOE, 1988)	ground - all N.D. (1 to 2) except 6.2 pg H_7CDD/g whole wt and 3 & 12 pg O_8CDD/g whole wt organ - all N.D.(1) except O_8CDD, ND(5) steak - all N.D.(1 to 3)-except 6,12 & 24 pg O_8CDD/g fresh wt	0.39 pg TEQ/g fresh wt
Pork - Limited Canadian data, 7 samples for fresh & cured pork (Ryan et al, 1985)	fresh - all ND (1 to 6) except 1.1 pg H_6CDD/g fresh wt, 3.6 pg H_7CDD/g fresh wt cured - all ND (1) except 1.6 and 2.6 pg H_7CDD/g fresh wt & 4.4 & 15 pg O_8CDD/g fresh wt	0.19 pg TEQ/g fresh wt (assume pork contains 25% fat)
Eggs - Limited Canadian data, 5 samples (Ryan 1987, MOE, 1988)	All ND (1-6) except 8.8 pg H_7CDD/g fresh wt, 8,18 and 44 pg 0_8CDD/g fresh wt, 5 pg H_6CDF/g fresh wt, 7 pg H_7CDF/g fresh wt & 12 pg 0_8CDF/g fresh wt	0.84 pg TEQ/g fresh wt
Milk/Dairy - Limited Canadian data, 8 samples (Ryan 1987, MOE 1988)	All ND (0.1 to 8) except 0.43 pg H_7CDD/g fresh wt & 1 pg O_8CDD/g fresh wt	0.07 pg TEQ/g fresh wt (assume milk and dairy products are on average 3% fat)
Fruit,Apples & Peaches from Ontario (5 samples) apple and Pear composite (Ryan, 1987)	All ND (0.1 to 2) except 0.6, 7, 8 & 46 pg 0_8CDD/g fresh wt	0.07 pg TEQ/g fresh wt
Vegetables - Potatoes and Tomatoes from Ont. (5 samples) vegetable fat sample (Ryan 1987, MOE 1988)	All ND (0.1 to 3) except 1, 3 and 3 pg O_8CDD/g fresh wt	0.05 pg TEQ/g fresh wt
Wheat-based Products - Wheat from Ontario (2 samples)(MOE 1988)	All ND (0.2 to 5) except 0.6 & 0.7 pg O_8CDD/g fresh wt	0.05 pg TEQ/g fresh wt

1 Calculations based on average detected value. **Where data are reported as non-detected (ND) or absent then residues assumed present at the minimum reported detection limit.** TEQ are derived using international TEF values (NATO-CCMS, 1988; CEPA, 1990)

2 U.S. and German food residue data also evaluated (Firestone et al, 1986; Beck et al, 1989)

Table 5: Multi-Media Exposure Estimate (1988)

Medium	Concentration in Medium		Estimated Intake (pg TEQ/kg body wt/d)
	Total PCDD/PCDF	Toxic Equivalents (TEQ)	
Air	mean: 5.3 pg/m^3 range: 0.4 - 36.7 pg/m^3	0.2 pg/m^3 0.03 - 0.91 pg/m^3	0.07
Water	range: ND - 46 pg O_8CDD/L	0.07 pg/L	0.002
Soil	mean: 2700 pg/g range: 50 - 14,100 pg/g	49 pg/g 1 - 330 pg/g	0.02
Consumer[1] Products	range: ND - 250 pg/g	15 pg/g	0.005
Food[2]	range: ND - 100.7 pg/g	0.0007 - 0.59 pg/g	1.8 - 2.3

1. based on bleached paper products only
2. including fish

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Chapter 6

Ambient Air Round Robins for PCDD/PCDF

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SUMMARY

Under the direction of the Canadian Council of the Ministers of the Environment (CCME), Environment Ontario and Environment Canada have carried out two round robin studies for PCDD/PCDF in ambient air. The first study involved a comparison of three samplers (two modified high volume samplers and a Model PS-1 low volume sampler) using teflon coated glass fibre filters and polyurethane foam plugs. Analytical methodologies were also compared in this study. Eight laboratories participated in the second round robin, which involved the analysis of exposed PUF/filter combinations, ambient air extracts and standards. A number of labs performed well in the round robin, but there was more variability between labs than had been expected, indicating the need for further method development.

INTRODUCTION

CCME is a joint provincial/federal steering committee with a mandate to sponsor joint research and development projects related to environmental priorities, such as toxic contaminants in air. A subcommittee to study PCDD and PCDF in ambient air was formed to develop sampling and analytical methodology for these compounds due the intense public interest in this set of compounds.

One of the important tasks involved in the development of any analytical method is the validation of the method by interlaboratory comparisons. The interlaboratory comparison allows one to determine the ruggedness of the method, the precision of the method, and the capability of the labs involved.

Sampling and analytical methods for PCDD and PCDF have been developed by Environment Canada and Environment Ontario over the past few years. Both Environment Canada and Environment Ontario have modified a standard high volume sampler by the incorporation of both a cartridge to house a polyurethane foam adsorbent and a dry gas meter to measure the volume of air drawn through the sample. Both samplers use teflon coated glass fibre filters

followed by a polyurethane foam plug. Experiments have been carried out to determine the efficiency of the samplers. This was done by spiking the filter and foam plug with $^{13}C_{12}$-PCDD and $^{13}C_{12}$-PCDF and then drawing air through the system. The recovery and the location of the spikes was monitored to determine breakthrough volumes. A sampler with a single PUF and 24-48 hour sampling was determined to be viable (1,2). Analytical methodology development was also carried out by both labs, based on the modification of existing PCDD/PCDF methods.

Round robins involving PCDD/PCDF analysis have previously been carried out for PCDD/PCDF standards (3), incinerator fly ash and stack emissions (4-7), pulp and paper samples (8-10), adipose tissue (11), water (12), and capacitor fluid (13). The development of methods for PCDD/PCDF in ambient air has been relatively recent and little has been reported on round robin validation of ambient air methods.

ROUND ROBIN #1: SAMPLING AND ANALYSIS INTERCOMPARISON (reference 14)

Objectives

The goals of the initial Environment Ontario/Environment Canada round robin study were to determine the variability between the two modified high volume samplers and a Model PS-1 low volume sampler and to ascertain if there was a difference in the analytical cleanup procedures of the two labs. Method precision and quality control/quality assurance practices were also to be determined.

Study Design

Two of each type of sampler mentioned above were co-located in a grassy area near a highway in metropolitan Toronto. Samples were collected for 24 hour periods on three separate days in the winter of 1987. Passively exposed field blanks were also collected before and after the sampling period. Environment Ontario analyzed samples from its modified high volume sampler and the PS-1 sampler and Environment Canada analyzed samples from their high volume sampler. The filter and PUF samples were extracted, cleaned and analyzed separately.

The detailed characteristics of the samplers used by Environment Ontario and Environment Canada are shown in Table 1. All samplers used teflon coated glass fibre filters but incorporated varying depths of foam plugs. Flow rates varied between the samplers, with Environment Canada's sampler having the highest flow rate.

Table 1: Sampler Characteristics for Intercomparison Study

	Environment Canada	Environment Ontario	Environment Ontario
Type	modified Hi-Vol	modified Hi-Vol	model PS-1
Filter	Pallflex - TX40H120WW teflon-coated GFF 20 x 25 cm	Pallflex - T60A20 teflon-coated GFF 20 x 25 cm	Pallflex - T60A20 teflon-coated GFF 10 cm diameter
Adsorbent	❑ polyurethane foam ❑ firmness factor: 31 ❑ density: 24.0 kg/m^3 ❑ size: 15 x 7.5 cm diameter	❑ polyurethane foam ❑ firmness factor: 30 ❑ density: 24.0 kg/m^3 ❑ size: 7.5 x 8.6 cm diameter	❑ polyurethane foam ❑ firmness factor: 30 ❑ density: 24.0 kg/m^3 ❑ size: 7.5 x 5.9 cm diameter
Flow Rate (L/min)	approx. 600	425-600	approx. 280
Volume (m^3/24 hr)	800-900	615-825	320-400
Flow Device	dry gas meter (temperature compensated)	rotameter	flow venturi magnehelic gauge

The foam cartridges were pre-cleaned using solvent before use. Exposed samples were stored in pre-cleaned foil placed in sealed plastic bags. All samples were stored in freezers prior to cleanup.

Analytical

The general cleanup methodology of the two laboratories was similar. The samples were spiked with isotopically labelled PCDD/PCDF surrogates prior to extraction. Toluene was used to Soxhlet the samples for 20 hours. The extract was concentrated and cleaned up using a series of columns (acid/base silica, silver nitrate silica and basic alumina) that were eluted with a series of solvents. The final extract was concentrated just to dryness and an isotopically labelled injection standard was added.

Both labs used a Finnigan 4500 HRGC/LRMS instrument in the electron impact mode. Environment Ontario used a SE-52XL column and Environment Canada used a DB-5 column. Mean detection limits obtained using the Finnigan 4500 LRMS were :

Environment Canada HiVol	0.06 pg/m^3 TCDD to 0.25 pg/m^3 OCDD
Environment Ontario HiVol	0.17 pg/m^3 TCDD to 0.40 pg/m^3 OCDD
Model PS-1	0.40 pg/m^3 TCDD to 0.65 pg/m^3 OCDD

Mean surrogate recoveries ranged from 70 to 79%for the Environment Canada sampler and 69 to 92% for Environment Ontario's sampler. These surrogate recoveries were used to correct all concentration data.

Results

The passive samples were determined to be clean with the exception of one Environment Ontario filter sample. The cause of the contamination was not determined.

Partial data from reference 14 are presented in this chapter (see tables 2 and 3). For full data set, please consult the reference. Also a number of the Environment Ontario samples were re-analyzed using HRMS. This resulted in a better comparison of the data between labs. The native PCDD and PCDF detected on the first day of active sampling in shown in Table 2. Only four congener groups were detected including HpCDD, OCDD, TCDF and HxCDF. All levels were below 1 pg/m^3. Variability between samplers was observed with the greatest difference in the HxCDF analysis. For some congeners, detection limits were near the levels of positives detected on some samplers precluded a good comparison.

Table 3 lists some of the congener groups detected on the third active day of sampling. Again some of the samples have been re-analyzed on HRMS. A very good comparison was observed for some of the isomers between samplers, although some within sampler variability was observed.

Table 2: Native PCDDs/PCDFs Detected in ACTIVE 1 Sampling

Congener (pg/m^3)	Environment Canada		Environment Ontario		Model PS-1	
	a	b	a	b	a	b
HpCDD	0.12	<0.13	<0.1	<0.2	<0.1	<0.09
OCDD	0.48	0.62	1.0	<0.4	<0.2	0.9
TCDF	0.09	0.10	<0.1	<0.1	<0.03	<0.09
HxCDF	<0.16	<0.16	0.9	0.4	<0.06	<0.06

Table 3: Native PCDDs/PCDFs Detected in ACTIVE 3 Sampling

Congener (pg/m^3)	Environment Canada		Environment Ontario		Model PS-1	
	a	b	a	b	a	b
HxCDD	<0.11	0.08	<0.06	0.5	0.2	0.5
HpCDD	0.78	0.64	1.4	0.7	0.2	0.6
OCDD	1.5	1.0	1.7	0.6	0.05	1.0
TCDF	0.15	0.04	<0.05	0.3	0.09	0.2
OCDF	0.17	<0.13	0.27	0.1	0.1	0.2

Conclusions

In general, low levels of PCDD and PCDF were detected in the active samples collected in Toronto and the congeners were generally detected on the filters as would be expected with winter sampling. The Environment Canada sampler had consistent results, low detection limits and good surrogate recoveries whereas the Environment Ontario sampler results had more variability and the PS-1 sampler had consistently higher detection limits due to lower sampling volumes.

ROUND ROBIN #2: ANALYTICAL METHOD INTERCOMPARISON (reference 15)

Objectives

After further analytical method development by the Environment Ontario and Environment Canada, another round robin study was initiated to determine the capability of Canadian laboratories for the analysis of PCDD/PCDF in ambient air. If a monitoring program were to be established, it would be important to know that different laboratories could provide comparable results.

Study Design

Seven modified high volume samplers were co-located at a site in Windsor, Ontario and ambient air samples (foam and filter) were collected for analysis by each laboratory. One sample provided to the labs consisted of a teflon-coated glass fibre filter/polyurethane foam plug pair that had been exposed for a 48 hour period. Each laboratory was also provided with a spiked extract. The extract represented the combined extracts from a number of PUFS and filters from the Windsor site. A number of native PCDD/PCDF were also added to

ensure that some positives were detected. The labs also received a blank PUF/filter pair, a low level spiked blank and an unknown standard mixture.

The participating laboratories included:

- ❑ Environment Ontario, Rexdale, Ontario
- ❑ Environment Canada, Ottawa, Ontario
- ❑ ELI ECO Laboratories, Rockwood, Ontario
- ❑ Mann Testing Laboratories, Mississauga, Ontario
- ❑ Novalab Ltd., Lachine, Quebec
- ❑ Wellington Environmental Consultants, Guelph, Ontario
- ❑ Zenon Environmental Laboratories, Burlington, Ontario

Analytical

Participants were instructed to use their own methodology for sample clean-up and analysis. The labs were also total to report total pg in the samples and pg/µL for the standards. Table 4 gives a detailed comparison of the methodologies used for clean-up and analysis. All samples were extracted using Soxhlet extraction, followed by clean-up with modified silica and alumina columns. Procedures and eluting solvents/volumes for the columns varied between the labs. Additional cleanup was sometimes performed using carbon packed columns. Instrumentation and surrogates used are also described in Table 4.

Results

The values determined by each lab for the exposed foam/filter samples are shown in Table 5. (Laboratories have been assigned random number identifiers.) The laboratories reported total pg and concentration calculations were made by Environment Ontario based on the known volume of air drawn by each sampler. Low levels of all congeners were detected, although not consistently between the labs, depending on detection limits and methodology. Wide ranges were observed within congener groups, between labs. When higher levels were detected, such as for HpCDD and OCDD, better agreement was obtained. Some of the variation may have occurred due to differences in exposure of the samples.

Due to the fact that there could have been variations in sampling, a pooled exposed extract was also provide to the labs to determine between lab precision. Results from this sample are shown in Table 6 in units of total pg determined in the sample provided. The extracts had also been spiked with 200 pg of 1,2,3,4-TCDD, 700 pg of HxCDD and 70 pg of HxCDF. Once again, a wide range of total pg values and number of congeners detected was seen. Again the best agreement observed was for the HpCDD and OCDD congeners where 300 to 700 pg were detected. Laboratories 3 and 5 did not detect the spiked congeners, even though the spikes were above their detection limits. The overall high detection limits of lab 5 indicated a problem. Five laboratories had generally acceptable agreement.

A low level spike containing three dioxin isomers was provided to determine the lower limits

detectable by the labs. Table 7 contains the results of this study. There is good agreement between the average value and the predicted spike level. Each laboratory was either consistently higher or consistently lower than the average value.

Table 8 shows the results for the unknown standard mixture provided to the participants. the expected values, the average values and corresponding standard deviations are also listed. There is close agreement between the expected values and the average values, with the exception of HpCDD. This may have been an error with the stock solution used to make up the mixture. Some laboratories had problems with some of the isomers. As a part of water round robin, the same unknown standard was provided to the same laboratories. A comparison of the average values obtained in each round robin is shown in Table 9. There is good agreement for the average values between round robins; however, it was noted that there sometimes was a large difference within a lab between round robins.

Conclusions

The capability for the analysis of PCDD/PCDD in ambient air samples was determined to be adequate for five of the seven participating labs. Further analytical methodology development and standardization is required to reduce the variability of results for these types of samples. Agreement on standard solutions indicates that the problems exist in the clean-up of the samples. The variability between co-located samplers also needs to be investigated.

A round robin with 18 participating labs and more replicate samples has been conducted since this workshop was conducted. Partial results from this study are shown in references 16 and 17.

Table 4: Methods Used for Round-Robin Study

	Environment Ontario	Environment Canada	ELI ECO	Mann Testing	Nova	Wellington	Zenon
CLEANUP							
Extraction	Soxhlet (toluene)	Soxhlet (toluene)	Soxhlet (toluene)	Soxhlet (toluene)	Soxhlet (toluene)	Soxhlet (toluene)	Soxhlet (CH_2Cl_2)
Column Cleanup	Modified Silica; Alumina	Modified Silica; Alumina	Modified Silica; Alumina	Modified Silica; Alumina	Modified Silica; Alumina	Modified Silica; Alumina	Modified Silica; Alumina
Carbon Cleanup	none	none	Carbon on Glass Fibre	none	Carbopack C on Celite	none	none
ANALYSIS							
Instrumentation	Finnigan TSQ-70	Finnigan 4500	HP 5970 (MSD)	Finnigan 4500	HP 5970 (MSD)	VG 12000	Finnigan TSQ-70
Final Sample Volume (uL)	10	20	20	50	10	10	25
Injection Volume (uL)	2	2	2	2.5	2	2	1
^{13}C-Surrogates Used	TCDD; PCDD; HxCDD; HpCDD; OCDD	TCDD; PCDD; HxCDD; HpCDD; OCDD; TCDF	TCDD; PCDD; HxCDD; HpCDD; OCDD	TCDD; OCDD	TCDD; OCDD	TCDD; PCDD; HxCDD; HpCDD; OCDD	TCDD; HxCDD; OCDD
Method of Quantitation	peak area	peak area	peak area	peak area	peak area	peak height	peak area

Table 5: Exposed GFF/PUF Results - Concentrations in pg/m^3

Laboratory Volume sampled (m^3)	1 1328	2 1118	3 1123	4 1442	5 1189	6 1292
Congener						
2,3,7,8-TCDD	NR	ND(0.02)	ND(0.04)	ND(0.04)	ND(0.07)	NR
TCDD	0.15^{8}	0.04^{1}	ND(0.04)	ND(0.07)	ND(0.07)	ND(0.05)
PCDD	0.28^{12}	ND(0.02)	ND(0.07)	ND(0.02)	ND(0.13)	ND(0.01)
HxCDD	0.52^{7}	0.28^{5}	ND(0.04)	0.22^{1}	ND	0.19^{3}
HpCDD	0.41^{2}	0.42^{2}	0.47^{2}	0.40^{2}	0.87^{2}	0.20^{2}
OCDD	0.74	0.43	1.4	0.22	0.84	0.48
2,3,7,8-TCDF	NR	0.12^{1}	0.08^{1}	0.04^{1}	ND(0.10)	NR
TCDF	INT	0.54^{9}	0.15^{3}	0.40^{10}	ND(0.10)	0.36^{14}
PCDF	0.83^{13}	ND(0.02)	0.07^{1}	0.36^{9}	ND(0.13)	0.60^{11}
HxCDF	0.61^{10}	0.38^{6}	ND(0.03)	ND(0.02)	ND(0.21)	0.48^{3}
HpCDF	0.36^{4}	0.23^{3}	ND(0.08)	0.03^{2}	ND(0.93)	0.12^{2}
OCDF	0.46	0.07	ND(0.07)	0.06	ND(0.26)	ND(0.08)

NOTE: **ND = not detected**
INT= interference
NR = not reported

Table 6: Spiked Combined Extract Results

LABORATORY	1	2	3	4	5	6	7
Congener							
2,3,7,8-TCDD	NR	ND(26)	ND(70)	ND(40)	ND(115)	NR	ND(29)
TCDD	150^{6}	220^{3}	ND(70)	356^{3}	ND(115)	69^{1}	71^{1}
PCDD	180^{12}	ND(25)	ND(91)	ND(12)	ND(115)	27^{1}	ND(52)
HxCDD	1000^{5}	670^{4}	ND(48)	412^{1}	540^{1}	600^{4}	530^{2}
PpCDD	300^{2}	370^{2}	325^{2}	491^{2}	ND	350^{2}	291^{2}
OCDD	329	390	598	315	700	440	384
2,3,7,8-TCDF	NR	ND(26)	84^{1}	114^{1}	ND(150)	NR	76^{1}
TCDF	420^{14}	160^{3}	205^{3}	448^{10}	ND(150)	260^{14}	90^{2}
PCDF	178^{10}	ND(25)	69^{1}	424^{8}	ND(115)	250^{9}	ND(41)
HxCDF	199^{5}	160^{3}	ND(30)	264^{1}	ND(190)	89^{2}	105^{2}
HpCDF	53^{2}	94^{1}	ND(47)	33^{2}	ND(2100)	55^{1}	61^{1}
OCDF	19	ND(52)	ND(43)	24	ND(410)	51	32

NOTE: Extracts spiked with 200 pg 1,2,3,4-TCDD, 700 pg HxCDD and 70 pg HxCDF
ND = not detected; INT = Interference; NR = not reported.

Table 7: Low Level Spike Results - Conc. in pg/µL

LABORATORY	1	2	3	4	5	6	7	Spike Level	Average (S.D.)
Congener									
TCDD	7	8	18	9	11	17	9	12	11(4)
HxCDD	13	16	ND(6.3)	9	16	21	20	20	16(4)
OCDD	24	18	41	11	25	33	26	29	25(10)

Table 8: Unknown Standard Results - Conc. in pg/µL

LABORATORY	1	2	3	4	5	6	7	Expected Values	Average (S.D.)
Congener									
TCDD	87	81	136	113	100	160	101	100	111(28)
PCDD	89	80	132	73	66	95	92	100	90(21)
HxCDD	180	170	189	89	130	170	151	160	154(35)
HpCDD	82	110	141	99	130	100	107	200	110(20)
OCDD	200	190	227	100	190	200	189	200	185(40)
TCDF	39	39	51	40	68	45	42	50	46(11)
PCDF	46	41	58	37	51	59	41	50	48(9)
HxCDF	71	72	102	61	100	98	72	80	82(17)
HpCDF	98	78	100	70	200	80	93	100	94(57)
OCDF	84	79	110	46	134	140	83	100	97(33)

Table 9: Comparison of Average Unknown Standard Values Obtained in Two Independent Round Robins (pg/µL)

CONGENER	EXPECTED VALUES	AIR ROUND-ROBIN AVERAGE VALUES (n = 7 labs)	WATER ROUND-ROBIN AVERAGE VALUES (n = 6 labs)
TCDD	100	111 ± 28	113 ± 28
PCDD	100	90 ± 21	93 ± 20
HxCDD	160	154 ± 35	169 ± 53
OCDD	200	110 ± 20	117 ± 50
	200	185 ± 40	201 ± 38
TCDF	50	46 ± 11	48 ± 8
PCDF	50	48 ± 9	50 ± 4
HxCDF	80	82 ± 17	87 ± 13
HpCDF	100	94 ± 57	120 ± 51
OCDF	100	97 ± 33	102 ± 25

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Chapter 7

Data Interpretation and QA/QC

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INTRODUCTION

Numerous state environmental agencies have required ambient monitoring of 2,3,7,8 substituted PCDDs/PCDFs (Table 1) in the vicinity of potential PCDDs/PCDFs sources (e.g. municipal solid waste incinerators) and in areas of high population density to determine compliance with ambient PCDDs/PCDFs standards and guidelines. In response to this, ENSR Consulting and Engineering has utilized sampling and analytical methodology employing high volume sorbent samplers in concert with high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) to determine ambient PCDDs/PCDFs concentrations in the 0.01-0.1 pg/m^3 range at several locations in the continental United States.

Accordingly, an extensive Quality Assurance/Quality Control framework is warranted to establish the validity and applicability of ambient PCDDs/PCDFs data. QA/QC features utilized in our ambient PCDDs/PCDFs monitoring programs include field surrogate recoveries, collocated samples, field blanks, laboratory internal standards, and laboratory method blanks, as summarized in Table 2, and discussed further in this section. Additional QA/QC data collected beyond the ambient PCDDs/PCDFs database discussed herein follows the data trends and findings identified in this section.

SAMPLING AND ANALYSIS METHODOLOGY

General Metal Works Polyurethane Foam (PUF) PS-1 samplers were used to collect the PCDDs/PCDFs isomers listed in Table 1. The samplers are essentially modified high volume air samplers employing a glass fibre filter in tandem with a sorbent trap to collect particulate-associated and vapour-phase PCDDs/PCDFs, respectively. Air flow rates between 140 and 220 lpm were utilized in conjunction with 24 to 96 hour sample sessions to produce sample volumes between 350 m^3 and 950 m^3. All PS-1 samplers were calibrated prior to and at the conclusion of each sampling session using an NBS traceable calibrated orifice.

All program samples selected for analysis were prepared and analyzed based on the protocol

outlined in EPA Methods 8280 and 8290. Native dioxins and furans collected from the ambient air were quantified against isotopically labelled internal standards added to each sample prior to extraction with toluene. Extracts were cleaned by column chromatography and subjected to complete PCDDs/PCDFs analyses by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). Detection limits of 10 to 50 fg/m^3 were achieved.

TABLE 1: Target Parameter Listing

	PCDDs		PCDFs
Total TCDD	2,3,7,8-TCDD	Total TCDF	2,3,7,8-TCDF
Total PeCDD	1,2,3,7,8-PeCDD	Total PeCDF	1,2,3,7,8-PeCDF
			2,3,4,7,8-PeCDF
Total HxCDD	1,2,3,4,7,8-HxCDD	Total HxCDF	1,2,3,4,7,8-HxCDF
	1,2,3,6,7,8-HxCDD		1,2,3,6,7,8-HxCDF
	1,2,3,7,8,9-HxCDD		2,3,4,6,7,8-HxCDF
			1,2,3,7,8,9-HxCDF
	1,2,3,4,6,7,8-HpCDD	Total HpCDF	1,2,3,4,7,8,9-HpCDF
	OCDD		OCDF

TABLE 2: Summary of Quality Assurance/Quality Control Elements

QA/QC Element	Purpose
Field Blank	Field/Laboratory Contamination
Method Blank	Laboratory Contamination
Field Surrogates	Analyte Retention and Method Accuracy
Internal Standards	Sample Validation
Collocated Samplers	Precision

QUALITY ASSURANCE/QUALITY CONTROL ELEMENTS

Field Blanks

Field blanks are collected and analyzed to assess possible contamination derived from the sampling and analysis process. Field blanks are randomly selected in the field from the population of clean, prepared PUF/filter sampling cartridges, and opened to the atmosphere for the duration of the sample set-up and recovery period (approximately 10 minutes). Each blank is also placed into and removed from a sampler head to mimic the procedure implemented for actual samples. Analytical results reported for actual samples were corrected using the corresponding field blank to more accurately assess native ambient levels of PCDDs/PCDFs by subtracting any congener quantity detected in the field blank from the amount detected for that same congener in the sample.

Method Blanks

Quality control procedures implemented for our ambient PCDDs/PCDFs monitoring programs also included the analyses of blank PUF sample cartridges which were pretreated and processed through the sample preparation procedures in a fashion identical to program samples. Analytical results obtained from these method blanks provide verification of sorbent clean-up, as well as means of detecting spurious contamination introduced in the laboratory.

Field Surrogates

Prior to sample collection, PUF sorbent cartridges were spiked with at least three isotopically labelled PCDDs/PCDFs from those identified in Table 3. The surrogate compounds were spiked just below the inlet surface of the PUF plug at the laboratory following completion of the clean-up procedure and prior to disposition to the field team.

TABLE 3: Field Surrogates Data Statistical Summary

	50 pg Spike % Recovery (n=3)		200 pg Spike % Recovery (n=3)		500 pg Spike % Recovery (n=70)	
Compound	**mean**	**Std. Dev.**	**mean**	**Std. Dev.**	**mean**	**Std. Dev.**
^{37}Cl-TCDD	110	8.1	84.6	9.3	105	21.8
$^{13}C_{12}$-TCDF	112	15.6			97.7	15.6
$^{13}C_{12}$-PeCDF			108	12.5		
$^{13}C_{12}$-HxCDF	103	6.4	109	13.8		
$^{13}C_{12}$-HxCDD			109	20.9	95.2	26.2
$^{13}C_{12}$-HxCDF			85.3	15.6		

Laboratory Internal Standards

Isotopically labelled PCDDs/PCDFs internal standards were spiked into each PUF cartridge just prior to soxhlet extraction. Their recoveries allowed for quantitation of target parameters and field surrogates. Table 4 lists the internal standards applied and the congener class quantitated by each.

TABLE 4: Laboratory Internal Standards

Quantitated Analytes	Internal Standard
TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
PeCDDs and PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
HxCDDs and HxCDFs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
HpCDDs and HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD and OCDF	$^{13}C_{12}$-OCDD

Collocated Samplers

Collocated sampler pairs are used to establish precision of the combined sampling and analysis regime. Collocated samplers are operated for an identical duration at nearly identical flow rates and are located close enough to each other so as to represent the same ambient air conditions without causing interferences with each other.

QA/QC DATA SUMMARY

Field blank data indicate that field-derived and laboratory contamination pose minimal impact on program samples for tetra, penta and hexa-substituted PCDDs/PCDFs as reflected by infrequent detection (less than 15%) of Cl_4, Cl_5 and Cl_6 substituted congeners in field blanks. Occasional measured levels for hepta and octa dioxins and furans in field blanks may suggest the influence of passive particulate on field blanks as well as program samples. The method blank population (n=22) with low frequency of detection for all congeners, also indicates that laboratory contamination does not regularly impact program samples.

Field surrogate recoveries for six isotopically labelled compounds applied at three fortification levels (50 pg, 200 pg, and 500 pg) are listed in Table 3. Results show average recovery for all surrogates across all fortification levels is 99%, indicating acceptable accuracy for the programs. Based on these recovery data, there appears to be no relation between average

surrogate recovery and surrogate compound nor an established dependence of average surrogate recovery on fortification level. These findings indicate that a surrogate cocktail containing several selected PCDDs/PCDFs isotopes is effective for monitoring and confirming analyte retention of all target compounds. Field surrogate and internal standard recoveries from individual samples are compared to average recoveries established by the database. Any individual recovery value lying outside plus or minus two standard deviations from the mean recovery for that standard is considered an outlier, and data from that sample discounted.

An examination of our collocated sampler database (n=28) shows that the average precision for all measured comparisons are within the precision goal of 50% established at the program outset. Further, examination of the collocated sampler database shows precision (percent difference) to improve with increasing PCDDs/PCDFs concentration. Data pairs with measured values near the detection limit show precision values approaching the precision goal of 50%, while congener pairs measured at levels five to ten times the detection limit show improved precision approaching 25%.

Chapter 8

Database of PCDD/PCDF Levels in Ambient Air

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SUMMARY

A computerized database was prepared that included ambient air levels of PCDDs and PCDFs as well as methods used. This database will be updated periodically and will be used to identify where air contamination truly does exist and to help set regulatory limits.

INTRODUCTION

Wellington Environmental Consultants (Wellington) was contracted to develop a database for ambient air levels of PCDDs and PCDFs. The work was funded by the Canadian Council of Resource and Environment Ministers (CCREM) and administered by the Ontario Ministry of the Environment (MOE).

METHODOLOGY

This database was developed in concert with a similar database for PCDDs and PCDFs in pulp and paper and related samples. There were three tasks involved in this development:

A. Computerized Literature Search. A computerized literature search of the following databases was completed: Paperchem, Enviroline, Pollution Abstracts and Chemical Abstracts. This search used a selected list of keywords to identify published results based on the title and subject matter of the articles. The most current 15 years of literature were reviewed.

B. Surveys. Efforts were made to directly contact researchers at two recent conferences: the 1988 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, May 1988, Raleigh, North Carolina; Dioxin 1988, Eighth International Symposium on Chlorinated Dioxins and Related Compounds, August 1988, Umea, Sweden.

C. Database Development. All database programming was performed using dBase III Plus, version 1.1 (Ashton-Tate). The entire database is comprised of six separate sub-files: "CONTACTS" (known researchers); "REFER" (literature references); "AA METHOD" (ambient air methods); "AA LEVEL" (ambient air levels); "PP METHOD" (pulp & paper methods); and "PP LEVEL" (pulp & paper levels). By subdividing the data pool into six categories, the integrity of each record is more readily maintained and search/report procedures proceed at a faster rate.

Each of the six separate sub-databases is cross-referenced by an "entry code" field. This unique alphanumeric descriptor is based upon the last name of the questionnaire respondent or author of the article,and permits linking of the databases by using the dBase III+ "view" utility.

RESULTS

A. Sources of Information

Approximately 50 literature references were retrieved by computer search; 23 of these were found to be of direct use to the project. Of the detailed surveys, only 36 were returned. Over half of the survey respondents indicated that their organizations had the capability of dioxin/furan determination in ambient air and/or samples derived from the pulp & paper industry. However, in many instances data were not provided with the survey responses. Approximately 25% of the of the 41 general information sheets returned indicated some degree of dioxin capability.

B. Ambient Air Methods

Thirty-five responses were entered into the ambient air methods database. The most commonly used sampling systems involved glass fibre filters, polyurethane foam, XAD, or silica gel. A variety of cleanup methods were described and in most cases (27 responses) spiking was performed prior to extraction.

Data were most often produced as congener group totals (29 responses) and 19 laboratories indicated isomer-specific capabilities. Quadrupole instruments were predominantly used (17 responses) and 11 laboratories used magnetic sector mass spectrometers.

C. Ambient Air Levels. The data presented in Table 1 represent the ranges and means for the true ambient data (i.e. those data points which were indicated as not being adjacent to a potential source).

Table 1: Mean Ambient Air Levels (pg/m^3)

A. Chlorinated dibenzo-p-dioxins				
Congener Group	**# data pts**	**Low Value**	**High Value**	**Mean**
tetra	15	0.0007	0.44	0.12
penta	19	0.0100	1.09	0.19
hexa	32	0.0100	2.07	0.35
hepta	34	0.0400	5.11	0.80
octa	37	0.0640	8.60	1.55
B. Chlorinated dibenzofurans				
Congener Group	**# data pts**	**Low Value**	**High Value**	**Mean**
tetra	30	0.0120	7.50	1.09
penta	28	0.0100	5.00	0.63
hexa	30	0.0100	9.70	0.72
hepta	31	0.0100	14.00	1.14
octa	25	0.0100	7.50	0.62

Note: All data points in above table are from areas not adjacent to potential PCDD/PCDF sources.

DISCUSSION

It is obvious that this database would be quite valuable, but only if it contained sufficient data to be truly representative. There has to be more incentive for research groups and private laboratories to release their data.

It is strongly advised that this database be taken over by an international organization or agency with the authority to solicit such data.